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Chemical Speciation of Long-lived Radionuclide Technetium-99 and its Environmental Behaviour

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Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):

Shi, K., Hou, X., Roos, P., & Wu, W. (2012). Chemical Speciation of Long-lived Radionuclide Technetium-99 and its Environmental Behaviour. DTU Nutech.

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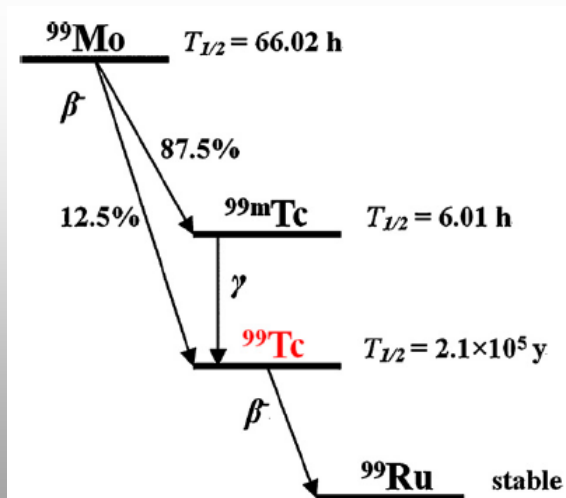
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Chemical Speciation of Long-lived Radionuclide Technetium-99 and its Environmental Behaviour

PhD-Report



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DTU-PhD
October 2012



Thesis for the Degree of Doctor of Philosophy
Center for Nuclear Technologies,
Department of Chemistry, Technical University of Denmark

Chemical speciation of long-lived radionuclide technetium-99 and its environmental behaviour

Keliang Shi

To be presented with the permission of the Department of Chemistry for public criticism in DTU,
Roskilde, Denmark on 29th October, 2012.

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Abbreviations

AMS	accelerator mass spectrometry
CF	concentration factor
EARP	enhanced actinide removal plant
EDTA	<u>e</u> thyl <u>e</u> di <u>a</u> mine <u>t</u> etra <u>a</u> cetic
EXAFS	extended X-ray absorption fine structure
HC	holding coil
HPLC	high performance liquid chromatography
ICP-MS	inductively coupled plasma mass spectrometry
LSC	liquid scintillation counter
NAA	neutron activation analysis
PUREX	<u>p</u> luto <u>n</u> ium <u>u</u> ranium <u>r</u> eco <u>v</u> ery by <u>e</u> xtraction
RIMS	resonance ionization mass spectrometry
SC	separation column
SD	standard deviation
SERS	surface enhanced raman spectrometry
SI	sequential injection
SP	syringe pump
SV	selection valve
TBP	<u>t</u> ri- <u>b</u> utylphosphate
TEVA	<u>t</u> etra <u>v</u> alent <u>a</u> ctinides
TIMS	thermal ionization mass spectrometry
TiOA	<u>t</u> ri- <u>i</u> so- <u>o</u> ctyl <u>a</u> mine
UV	<u>u</u> ltr <u>a</u> violet
XAS	X-ray absorption spectrometry

Resume

På grund af højt fissionsudbytte, høj mobilitet og lang halveringstid anses technetium-99 for at være blandt de vigtigste radioaktive isotoper til sporstofanvendelser i havmiljøet og at have væsentlig betydning i forbindelse med radioaktivt affald. Undersøgelser af metoder til at bestemme technetium og dens kemiske former er derfor vigtige for at forstå, hvorledes technetium opfører sig i miljøet. Denne afhandling sigter mod at udvikle analytiske metoder til hurtig og præcis bestemmelse af den samlede mængde ^{99}Tc i miljøprøver (f.eks. makroalger, jord og havvand) samt bestemmelse af kemiske former, som technetium forekommer på i makroalger. Afhandlingen omfatter desuden anvendelser af ^{99}Tc som et oceanografisk sporstof til at undersøge havstrømme og havforurening i kystområder ved at bruge makroalger som bioindikator.

Analytiske metoder til at bestemme ^{99}Tc i forskellige miljøprøver så som makroalger og havvand er blevet etableret. Metoder til forbehandling af forskellige prøvetyper er blevet undersøgt omfattende foraskning, syreoplukning af faste prøver samt fældning af technetium med jernhydroxid for store prøver af havvand. En ny fremgangsmåde er udviklet til at separere og oprense technetium fra prøvematrixer og interferende stoffer med efterfølgende bestemmelse af ^{99}Tc ved induktivt koblet plasma massespektrometri (ICP-MS). Stabiliteten af technetium ved tør-foraskning af faste prøver og våd-foraskning af væskeopløsninger af prøver er undersøgt i lys af de særlige kemiske egenskaber ved technetium, og herved er procedurer til forbehandling blevet fastlagt. Teknikker til ekstraktions-kromatografi med TEVA-kolonner er anvendt til at fjerne interferenser af rutenium og molybdæn. Det er blevet undersøgt, hvorledes technetium, rutenium og molybdæn fæstnes på og udtrækkes fra TEVA jonbyttere, og i forbindelse hermed er en mulig mekanisme til at kontrollere fæstelse af TcO_4^- ved forskellige koncentrationer af H^+ blevet afledt. Med brug af to små TEVA-kolonner (1.5 mL hver) er der for miljøprøver opnået dekontaminationsfaktorer på over 10^4 for molybdæn og over 10^5 for rutenium samt genfindning af technetium på 60-95%. Med ICP-MS analyseteknik er opnået en detektionsgrænse på 1.5 mBq for ^{99}Tc . De analytiske metoder har vist sig at være pålidelige og er anvendt med succes til analyser af miljøprøver.

En analysemetode til at bestemme kemisk speciering af ^{99}Tc i makroalger er blevet udviklet. Forskellige kemiske former for technetium blev separeret med biokemiske teknikker og bestemt med ICP-MS efter forbehandling af prøver og oprensning af technetium med ekstraktions-kromatografiske teknikker. Ud over TcO_4^- blev der fundet mest technetium i makroalgernes bio-makromolekyler så som algin, pigment, cellulose mm. Forskellige bindinger af technetium med disse bio-makromolekyler blev udledt.

Sæsonbetingede variationer i koncentrationer af ^{99}Tc i makroalger (*Fucus*) blev undersøgt ved at analysere månedlige tangprøver indsamlet ved danske kyster. Mulige årsager til disse sæsonvariationer blev undersøgt. Koncentrationsfaktoren for overførsel af technetium til makroalger blev fundet at være konstant og ikke variere med tidspunkt for indsamling. Resultaterne indikerer, at makroalger kan

anvendes som en pålidelig bioindikator til at overvåge niveauer af ^{99}Tc i havvand og til at vurdere tidsmæssige variationer samt spredning af forurening i marine systemer.

Abstract

Because of the high fission yield, high mobility and long half-life, technetium-99 is considered to be one of the most important radionuclides in environmental trace application as well as nuclear waste management. The study on the determination of technetium and its speciation is therefore a key issue for understanding its fate and behaviour in ecosystem. This thesis aims to develop series of analytical methods for rapid and accurate determination of total ^{99}Tc in environmental samples (e.g., seaweed, soil, and seawater), as well as speciation analysis of ^{99}Tc in seaweeds. The application of ^{99}Tc as an oceanographic tracer to investigate seawater movement and coastal pollution using seaweed as a bio-indicator was also investigated.

Analytical methods of ^{99}Tc for different environmental samples such as seaweed and seawater were established. According to the types of sample, different pre-treatment methods including dry ashing and acid leaching for solid samples as well as co-precipitation of technetium using ferrous hydroxide from large volume water samples were investigated in details and a novel approach has been developed to separate and purify technetium from sample matrix and other interferences prior to measurement of ^{99}Tc by inductively coupled plasma mass spectrometry (ICP-MS). Considering the special chemical property of technetium, the stability of technetium during dry ashing of solid samples and evaporation of sample solution was investigated and the corresponding pre-treatment procedures were proposed. To remove the interferences of ruthenium and molybdenum, extraction chromatographic techniques using TEVA column was applied. The sorption and elution behaviours of technetium, ruthenium and molybdenum onto TEVA resin were investigated and a possible mechanism controlling TcO_4^- sorption at different concentrations of H^+ was deduced. With the application of two small TEVA columns (1.5 mL for each), decontamination factors of $>10^4$ for molybdenum and $>10^5$ for ruthenium and recovery of 60-95% for technetium were achieved for different environmental samples. An absolute detection limit of 1.5 mBq for ^{99}Tc was obtained by ICP-MS measurement. The analytical methods were proved to be reliable and have been successfully applied for the determination of ^{99}Tc in environmental samples.

An analytical method for chemical speciation of ^{99}Tc in natural seaweed has been developed. Different species of technetium were separated using biochemical techniques and detected by ICP-MS after sample pre-treatment and purification of technetium using extraction chromatographic technology. Besides TcO_4^- , most of technetium was found in bio-macromolecules of seaweed, such as algin, pigment, celluloses, etc. Possible binding modes of technetium with these bio-macromolecules were deduced.

Seasonal variation of ^{99}Tc concentration in seaweed (*Fucus*) was investigated by analysis of seaweed samples collected monthly in Danish coast, and a possible mechanism driving its seasonal variation was explored. The concentration factor of seaweed to technetium was found to be a constant and does not vary with sampling date. The results indicate that seaweed can be used as a reliable bio-indicator to

monitor the level of ^{99}Tc in seawater and estimate the temporal variation and dispersion of pollution in the marine system.

Preface

This thesis was carried out at the Radioecology and Tracer Programme, Center for Nuclear Technologies, Department of Chemistry, Technical University of Denmark (DTU) during 2009-2012 in partial fulfilment of the requirements for acquiring the Ph.D degree in Chemistry.

The thesis mainly aims to establish analytical methods for rapid and accurate determination of total ^{99}Tc in environmental samples (e.g., seaweed, soil, and seawater), as well as speciation analysis of ^{99}Tc in seaweeds. The application of ^{99}Tc as an oceanographic tracer to investigate seawater movement and coastal pollution using seaweed as a bio-indicator was also investigated.

Roskilde, October 2012

Keliang Shi

Acknowledgements

I would like to express my gratitude to all those who helped me during the three years when I worked at Risø National Laboratory for Sustainable Energy as a Ph.D student.

A special acknowledgement should be shown to Senior Scientist Xiaolin Hou, my supervisor, who has been always supporting me with his wide knowledge, extraordinary patience and encouraging guide. His broad experiences and excellent ideas always refresh me. It is totally impossible to finish the Ph.D work without his kind help.

I am deeply grateful to Prof. Wangsuo Wu, who has guided me through the master studies and offered me the chance to continue my Ph.D study in Denmark. I thank Senior Scientist Sven P. Nielsen for giving me the opportunity to work in his group and encouraging me throughout the whole period of my Ph.D study. Senior Scientist Per Roos is greatly acknowledged for his great help on the operation of ICP-MS as well as the very kind comments during the experiment.

Dr. Jixin Qiao helped me a lot during the past three years. I hereby express my heartfelt thanks to her. Senior Scientist Kasper Grann Andersson gave me a number of constructive comments for my Ph.D research, is also sincerely acknowledged. I am grateful to my friends Luyuan, Yihong, Violeta, Haijun, Maoyi, Yukun, Peng-Yi, Peng-He, Jinfeng and Yali for their kind supports during my Ph.D study as well as the preparation of this thesis.

All my friends and colleagues in Center for Nuclear Technologies are warmly thanked and remembered for all the happy moments, good laughs, tricky discussion, and successful manoeuvre and co-operations. My friends Yixuan, Claus, Charlotte, Liga, Birgitte, Majbritt, Kristina, Susanne, Yusuf, Svend, and Lise have given me a lot of spirit needed for the work.

I should never forget to say thanks to my roommates, Mr. Qiang Hu, Mr. Jian Wu and Dr. Xiaofen Li, as well as all other friends from Risø, for the wonderful three years.

I should express my gratitude to my family. The love and care from my parents and other members of the family is always the source of power for my improvement. I should also say thanks to those who are in the brotherhood, for their effect on me to make who I am. My beloved wife Xiaoqing deserves sincere thanks, for the silent but irreplaceable help. Be with her, I can make all possible!

Finally, I expressed my gratitude to the partial financial support from China Scholarship Council to my PhD project.

List of papers related to this thesis

- I Shi, K.L., Hou, X.L., Roos, P., Wu, W.S. Determination of technetium-99 in environmental samples: A review. *Analytica Chimica Acta* 2012, 709, 1-20.
- II Shi, K.L., Hou, X.L., Roos, P., Wu, W.S. Stability of technetium and decontamination from ruthenium and molybdenum in determination of technetium-99 in environmental solid samples by ICP-MS. *Analytical Chemistry* 2012, 84, 2009-2016.
- III Shi, K.L., Qiao, J.X., Wu, W.S., Roos, P., Hou, X.L. Rapid determination of technetium-99 in large volume seawater samples using sequential injection extraction chromatographic separation and ICP-MS measurement. *Analytical Chemistry* 2012, 84, 6783-6789.
- IV Shi, K.L., Hou, X.L., Roos, P., Wu, W.S., Nielsen S.P. Seasonal variation of technetium-99 using *Fucus vesiculosus* as its application as oceanographic tracer. (submitted to *Estuarine, Coastal and Shelf Science*)

Contents

1. Introduction.....	1
1.1. Sources and distribution of technetium in the environment.....	1
1.2. Physicochemical property of technetium and its environmental behaviour.....	2
1.3. Analytical methods for determination of ^{99}Tc in environmental samples.....	4
1.3.1. Yield monitors for ^{99}Tc analysis.....	5
1.3.2. Sample pre-treatment.....	6
1.3.3. Chemical separation.....	7
1.3.4. Source preparation.....	9
1.3.5. ^{99}Tc measurement.....	9
1.4. Species of technetium.....	11
1.4.1. Behaviour of different technetium species.....	11
1.4.2. Techniques for speciation analysis of technetium.....	13
1.5. Research objectives.....	15
2. Experimental.....	16
2.1. Materials.....	16
2.2. Total technetium analysis.....	17
2.2.1. Sample pre-treatment.....	17
2.2.2. Separation of technetium using extraction chromatographic techniques.....	18
2.2.3. Source preparation.....	21
2.2.4. Measurement.....	21
2.3. Speciation analysis of ^{99}Tc	22
2.3.1. Chemical separation of technetium speciation in natural seaweed.....	22
2.3.2. Sample preparation and measurement.....	23
2.4. Rhenium analysis.....	24
3. Results and discussion.....	25
3.1. Stability of technetium	25
3.1.1. Loss of technetium during sample solution evaporation.....	25
3.1.2. Loss of technetium during solid sample dry ashing.....	27
3.2. Separation of technetium from sample matrix and main interferences.....	30
3.2.1. Co-precipitation of technetium from large volume seawater	30
3.2.2. Technetium separation and purification using extraction chromatography.....	31
3.3. Application of ^{99}Tc as an oceanographic tracer.....	34
3.3.1. Temporal variation of ^{99}Tc concentration in seaweed.....	35

3.3.2. Concentration factors.....	37
3.4. Chemical speciation of technetium in natural seaweed.....	39
3.4.1. Separation of various technetium species and their measurement	40
3.4.2. The behaviour of various technetium species in seaweed.....	44
4. Conclusions and perspective.....	47
References.....	49

1. Introduction

Technetium (Tc), element 43 in the seventh subgroup of the periodic table, is the lightest element with no stable isotope and is, therefore, extremely rare on the earth. It was first produced and isolated as a product from the bombardment of molybdenum (Mo) with deuterons by Perrier and Segre [1]. Up to date, 45 isotopes and isomers of technetium ranged from atomic masses of 85 to 117 have been synthesized, of which most are short-lived isotopes and a total of 10 isotopes with half-lives longer than 1 h (see **paper I**). Of the isotopes of technetium, technetium-99 (^{99}Tc) is the most environmentally important due to its long half-life ($T_{1/2} = 2.1 \times 10^5$ y) and high fission yield (6.1% for uranium-235 (^{235}U) and 5.9% for plutonium-239 (^{239}Pu)) [2].

The interest in investigating ^{99}Tc in the environment results partly from the absence of stable technetium isotopes. ^{99}Tc as the dominating isotope of technetium is thus the only isotope available for studying the environmental and biological behaviour of this element [3]. Due to its high mobility, high fission yield and long half-life, ^{99}Tc is considered to be one of the most important radionuclides in safety assessment of radioactivity in the environment, as well as in decommission of nuclear facilities and management of nuclear waste [4].

^{99}Tc in the environment is dominated by its releases from the nuclear fuel cycle, with most of them (> 90%) was directly discharged into the oceans from reprocessing plants in Europe [3]. The behaviour of technetium in the marine environment is significantly affected by redox conditions. In aerobic conditions such as open seas, technetium mainly exists as TcO_4^- and shows a high mobility and water solubility, which make ^{99}Tc an ideal oceanographic tracer for investigation of movement, exchange and circulation of water masses [5,6]. In anaerobic conditions, technetium can be reduced to low oxidation state such as Tc(IV), which is sparingly soluble and active to particles and strongly attaches in the subsurface of sediment [7,8].

Aquatic plants like brown seaweeds, especially *Fucus* genus, show high capabilities to accumulate technetium from seawater [9] and thus have been widely applied as biological indicators for monitoring the levels of ^{99}Tc in coastal regions [10,11]. Accordingly, an accurate and robust determination of ^{99}Tc in seaweed and seawater samples is needed. Furthermore, to explore the bioaccumulation mechanism of seaweed to technetium, the chemical speciation of technetium is necessary to be investigated. All of these, including the total technetium determination and technetium speciation analysis, will be helpful to understand the behaviour of technetium in the marine environment as well as in the ecosystem.

1.1. Sources and distribution of technetium in the environment

Technetium can be produced both naturally and artificially. In nature, ^{99}Tc is mainly produced by the spontaneous fission of ^{238}U , the neutron induced fission of ^{235}U has minor contribution [8]. A mass ratio of $^{99}\text{Tc}/^{238}\text{U}$ was found to be 10^{-12} in an enriched uranium-mineral sample, which gives an idea that it is difficult to characterize technetium by experimental way using the natural sources [12]. At present, almost all of ^{99}Tc in the environment results from anthropogenic nuclear activities, mainly

from nuclear weapons testing, reprocessing of spent nuclear fuel, nuclear accidents, nuclear power plants and medical application of ^{99m}Tc (see details in **paper I**). Among these, the releases from two European reprocessing plants at Sellafield (UK) and Cap de La Hague (France) are the main sources of ^{99}Tc in the environment, especially in the northern hemisphere. The discharge of ^{99}Tc from the La Hague reprocessing plant increased slowly from about 0.4 TBq/y in 1970 to a peak value of 25 TBq/y in 1985. By 1991 the discharges had fallen to 0.9 TBq/y and since then remained relatively stable at less than 1 TBq/y [10]. Compared to La Hague reprocessing plant, much more ^{99}Tc has been discharged from the Sellafield reprocessing plant. In the three-year period from 1978-1980, Sellafield discharged about 300 TBq of ^{99}Tc . From an average of 4-6 TBq/y throughout the entire 1980s, the discharges of ^{99}Tc increased to 190 TBq/y in 1995 because of the Enhanced Actinide Removal Plant (EARP) started in 1994 [13]. Although the amount of discharged ^{99}Tc decreased after 1995, the releases of ^{99}Tc from Sellafield is still the dominant source nowadays. Consequently, more than 90% of the anthropogenic ^{99}Tc in the environment is originated from these two reprocessing plants [3].

The human nuclear activities directly influence the distribution of ^{99}Tc in the environment. In some areas, especially in the contaminated environment near the sources, the levels of ^{99}Tc are relatively high. As the major sources of ^{99}Tc , Sellafield and La Hague reprocessing plants discharge ^{99}Tc mainly in liquid form which were directly released into the Irish Sea and English Channel, respectively. These ^{99}Tc (expected to be TcO_4^- form) are then transported to the North Sea and further northwards through the Norwegian Sea to the Arctic and the Greenland Sea. The water exchange between the North Sea and the Baltic Sea causes ^{99}Tc transport to the Baltic Sea. Seawaters in these areas are therefore highly contaminated and the concentration of ^{99}Tc is enhanced. Consequently, the concentrations of ^{99}Tc in aquatic plants (e.g. seaweed) and animals (e.g. shellfish) are usually higher in the contaminated environments than in uncontaminated areas [8]. Of course, the distribution features of ^{99}Tc are strongly influenced by the occurrence in different environmental compartment, such as atmosphere, terrestrial and marine environments and the concentrations of ^{99}Tc vary with the locations. Examples for the distribution of ^{99}Tc in some specific oceans, locations as well as sample types related to the anthropogenic nuclear activities are shown in **Paper I (Table 3)**.

1.2. Physicochemical property of technetium and its environmental behaviour

Technetium is a transition metal in the seventh subgroup of the periodic table, with a ground state electron configuration of $[\text{Kr}]4d^55s^2$. The closest chemical analogues of technetium are manganese (Mn) and rhenium (Re), and to a lesser degree the neighbouring elements molybdenum and ruthenium (Ru) [14]. However, technetium compounds appear to be more easily reduced than rhenium compounds and, accordingly, technetium compounds are frequently more reactive than their rhenium analogues. Technetium also differs from manganese, for example, in the high stability of the oxidation state of +7, in particular in the form of pertechnetate, compared to permanganate [2].

Technetium metal is silvery-gray and tarnishes slowly in moist air. It is easily dissolved by oxidizing acids like HNO_3 , aqua regia and concentrated H_2SO_4 , but is not soluble in any strength of HCl solution

[15]. In aqueous solutions, technetium can exist in different oxidation states of Tc(II), Tc(IV), Tc(V), Tc(VI) and Tc(VII), and each of them can be prepared under appropriate conditions. The Eh-pH diagram of technetium, calculated from thermodynamic data, indicates areas in which the various oxidation states of technetium are expected to predominate (Figure 1). Depending upon the redox conditions, technetium primarily exists in two oxidation states (Tc(VII) and Tc(IV)) in the environment. Under oxidizing conditions, technetium mainly exists as the pertechnetate ion (TcO_4^-) in aqueous solution or as volatile Tc_2O_7 in the absence of water [13]. Tc(IV) is the most stable oxidation state of technetium under reducing conditions and can be easily hydrolyzed in aqueous solutions. Relatively stable complexes of Tc(V) are formed in the presence of complexing reagents, and fluorination leads to the volatile TcF_6 [16]. In general, technetium species with oxidation states less than +4 are rapidly oxidized to Tc(IV) and ultimately to Tc(VII) in oxidizing conditions and those with oxidation states between +4 and +7 usually disproportionate quickly to corresponding mixtures of Tc(IV) and Tc(VII) [17].

TcO_4^- is a very common and important inorganic anion of technetium in the environment. It is stable in aquatic solutions over a wide range of pH in the absence of reducing substances. Unlike MoO_4^- , TcO_4^- has little tendency to form isopolyanions in environmental conditions [14]. As a weak oxidizing reagent, TcO_4^- can be reduced by reducing reagents such as sulphite, meta-bisulphite and ascorbic acid to a lower oxidation state [18,19]. The potential of the couple $\text{TcO}_4^-/\text{TcO}_2$ was reported to be +0.747 V in acidic aqueous solution [2]. Tc_2O_7 , an oxide of technetium with its highest valence, mainly exists in oxidizing conditions in the absence of water. It melts at 119.5 °C, boils at 311 °C and is very hygroscopic and dissolves in water to form pertechnetic acid (HTcO_4). Tc_2O_7 can be produced by dehydrating HTcO_4 on heating and easily volatilizes at high temperature. TcO_2 is the main oxide of technetium in low oxidation state. It is more thermodynamically stable, and is slightly volatile at 900 °C but does not decompose even up to 1100 °C [20]. Since TcO_2 remains insoluble in most aqueous conditions found in the natural environment, TcO_2 formation will be an important factor in the accumulation of technetium and any further diagenetic movement. Besides TcO_2 , various complexes of Tc(IV) can be formed in the presence of inorganic or organic ligands such as carbonate, ethylenediaminetetraacetic (EDTA) and natural humic substances, more details will be given in **species of technetium section**.

The behaviour of technetium in the environment is complex and mainly controlled by physical, chemical and biological processes. Once released in the liquid from the discharge points (e.g., Sellafield and La Hague reprocessing plants), ^{99}Tc can be dispersed by sea currents or concentrated by seaweeds or marine animals. Because of the high mobility (mainly in TcO_4^- form), long residence time in the ocean, long half-life of ^{99}Tc and low affinity of TcO_4^- to particulate matter and sediments in the oceans, ^{99}Tc has been widely used as an oceanographic tracer to track seawater movement and coastal pollution [10,21,22]. The uptake of technetium by aquatic plants and marine animals from contaminated seawater is the dominating way for ^{99}Tc to enter the food chains. Seaweeds, especially brown seaweeds like *Fucus* genus show very high capacities to accumulate ^{99}Tc from seawater (a

concentration factor of more than 1×10^5 was reported for *Fucus vesiculosus* [23]) and thus have been widely used as biological indicators for monitoring the levels of ^{99}Tc [11]. Aquatic animals such as snails, fish and shellfish (especially lobster) usually express relatively high abilities for technetium uptake. The accumulation of technetium by these organisms is related to their feeding habits and the concentration of technetium in the food sources [7]. Besides the distribution of ^{99}Tc in the marine environment, ^{99}Tc can also be released and dispersed into the air from the atmospheric nuclear weapons testing or nuclear accidents such as the Chernobyl and Fukushima accidents and then return to the earth via dry and wet deposition [24]. Accordingly, the uptake of ^{99}Tc by terrestrial plants from soil might be another way to introduce ^{99}Tc into the food chains. After death and decay of plants and animals, ^{99}Tc might accumulate in sediments or return to water, soil and other media for further cycling. A possible cycle of ^{99}Tc in the ecosystem has been shown in **Paper I (Figure 3)**.

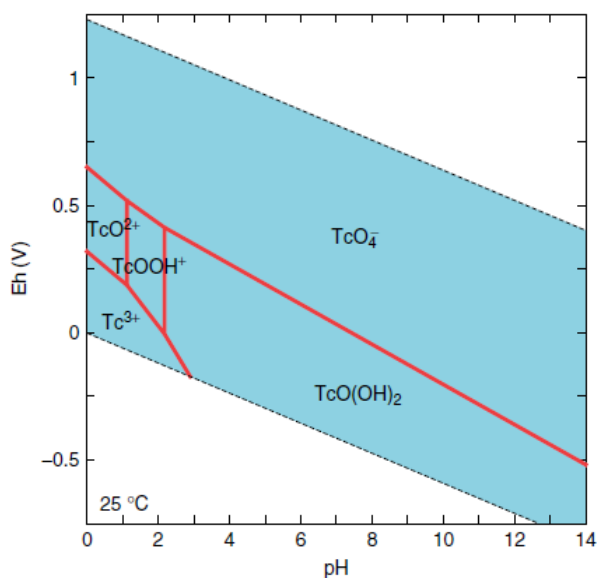


Figure 1. Eh-pH diagram of technetium obtained at 25 °C in aqueous media without other complexing reagents and adopted from reference [13].

1.3. Analytical methods for determination of ^{99}Tc in environmental samples

To investigate the behaviour of ^{99}Tc in the environment, an accurate and reliable determination of ^{99}Tc in different environmental samples is needed. So far, a large number of analytical methods have been developed and applied for the determination of ^{99}Tc in various environmental samples, such as soil, sediment, seaweed, seawater, groundwater and nuclear waste [18,19,25-29]. In general, the whole analytical procedure, as presented schematically in Figure 2, can be divided into four steps: sample pre-treatment, chemical separation, source preparation and ^{99}Tc measurement. A detailed discussion on these analytical procedures is presented below.

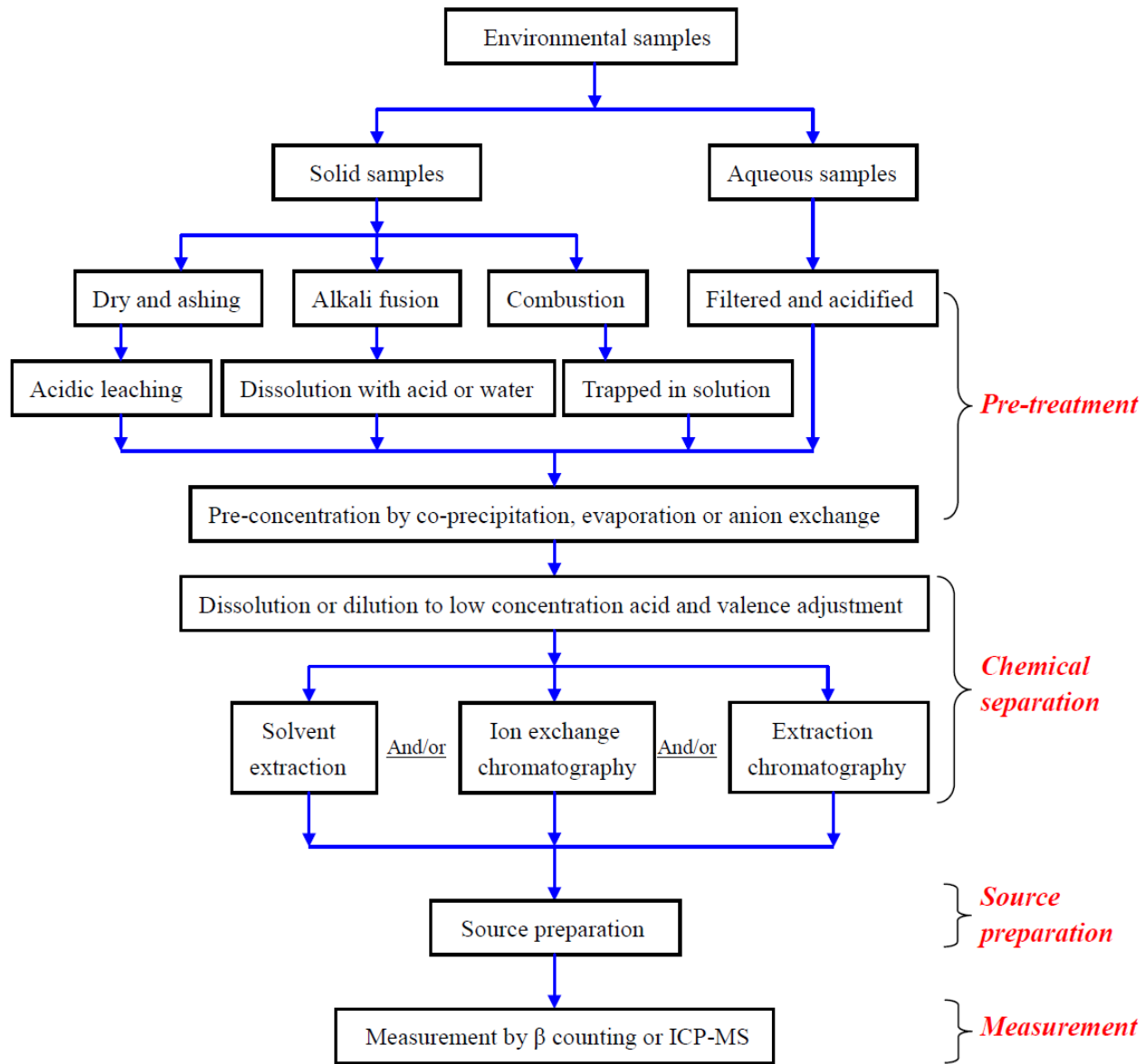


Figure 2. A general flow chart for determination of ^{99}Tc in environmental samples

1.3.1. Yield monitors for ^{99}Tc analysis

Because of the relatively low levels of ^{99}Tc in the environment, an extensive chemical separation is always required to concentrate ^{99}Tc from samples and to remove matrix components and interferences. The measurement of the chemical yield of ^{99}Tc during the whole analytical procedure is a key issue for obtaining accurate analytical results. Several yield monitors can be used for the analysis of ^{99}Tc , including isotopic tracers such as $^{95\text{m}}\text{Tc}$, $^{97\text{m}}\text{Tc}$, ^{97}Tc , ^{98}Tc and $^{99\text{m}}\text{Tc}$, as well as stable and radioactive

isotopes of rhenium, which is regarded as an analogue of technetium. Among these, ^{95m}Tc and ^{99m}Tc are the two commonly used yield tracers (see details in **Paper I**).

1.3.2. Sample pre-treatment

Sample pre-treatment normally aims to release and/or pre-concentrate the target analytes from environmental samples prior to the chemical separation and purification. Different pre-treatment methods can be utilized for the sample preparation according to the types of sample. For solid samples (e.g., soil, sediment, and seaweed), before chemical separation, ^{99}Tc needs first to be released from the sample matrix into solution. Dry ashing combined with acid digestion, alkali fusion following dissolution with water or diluted acid, and combustion at high temperature (e.g., $>900\text{ }^{\circ}\text{C}$) and trap technetium species in water or alkali solution are commonly used methods (see details in **Paper I**). Among these, dry ashing combined with acid digestion is the most convenient method for releasing of ^{99}Tc from solid samples, especially when dealing with large amount of samples (e.g., $>10\text{ g}$ soil or seaweed). The main challenge of this method is the complete decomposition of organic matter in the sample and the stability of technetium during heating [27,26,30]. Technetium is stable at relatively low ashing temperature (e.g., $<500\text{ }^{\circ}\text{C}$), but the organic matter in solid samples, especially in seaweeds (the amount of organic matter is about 80%), are difficult to completely decompose at low temperatures, which leads to a poor yield of ^{99}Tc after acid leaching [26]. On the contrary, if the ashing temperature is too high (e.g., $>800\text{ }^{\circ}\text{C}$), technetium will be lost through formation of volatile species and causes low yield of ^{99}Tc . Actually, the principle of oxidizing combustion method for technetium is mainly based on the unstable properties of technetium species at high temperature [31]. Accordingly, a comprehensive investigation of the ashing conditions for solid samples becomes necessary. After the complete decomposition of organic matter, acid solutions, such as concentrated HNO_3 , 8 mol/L HNO_3 or 3 mol/L $\text{HCl} + \text{H}_2\text{O}_2$, can be utilized to leach technetium from the ashed sample under heating and reflux on a hot plate at $70\text{--}125\text{ }^{\circ}\text{C}$ prior to further pre-concentration using co-precipitation or anion exchange chromatography.

For aqueous samples (e.g., seawater, rain water, and groundwater), because of the low level of ^{99}Tc , the samples usually require pre-treatment to pre-concentrate technetium. The enrichment of ^{99}Tc can be achieved by a few approaches, including evaporation [32], activated carbon adsorption [33], co-precipitation [34,35] and anion exchange chromatography [19] according to the volume and salinity of the samples. Evaporation is a simple method but can be adopted mainly for samples with a relatively small volume and low salt contents such as fresh water. Furthermore, because of the volatile properties of several technetium species, the evaporation of sample solution should be carried out at relatively low temperature (e.g., $<200\text{ }^{\circ}\text{C}$), resulting in a long pre-treatment time in most case. Because of the large specific area ($400\text{--}1600\text{ m}^2/\text{g}$), activated carbon can effectively adsorb technetium from water samples in a short time [33]. However, to release the adsorbed technetium from activated carbon, a dry ashing at high temperature is usually needed, which will cause some loss of technetium and also prolong the analytical time. So far, co-precipitation and anion exchange chromatography are the two commonly used methods to concentrate technetium from large volume water samples (see details in **Paper I**).

Compared with the anion exchange method, co-precipitation is relatively rapid and the problems with column blocking can be avoided when analyzing samples even after a long storage time. The most attractive advantage of this method is that it is very suitable for the pre-concentration of ^{99}Tc in the field (or on board a sampling vessel), which significantly reduces difficulties in transporting large volume water samples. However, to obtain a high chemical yield of technetium, a large amount of iron is often added to the sample solution, resulting in a bulky iron hydroxide precipitate, which might cause difficulties in the following separation stages. Accordingly, an optimized procedure for dealing with large volume of water samples using co-precipitation is still needed.

1.3.3. Chemical separation

The accuracy and precision of an analytical method for determination of ^{99}Tc to a large degree rely on the level of removal of interferences and matrix components. Due to the low concentration of ^{99}Tc in the environment, a large sample is normally required for analysis to obtain sufficient signal, which in turn increases the amount of interferences and matrix components in the sample solution. The main potential interferences for the measurement of ^{99}Tc by radiometric and spectrometric methods have been listed in **Paper I (Table 6)**. The method adopted for chemical separation of technetium should not only result in good decontamination from interferences but also provide a high chemical yield of technetium. For separation and purification of technetium, a variety of techniques have been used, yet the most common ones are solvent extraction, anion exchange chromatography, extraction chromatography or a combination of two or more methods [18,27,36,37].

Solvent extraction

Solvent extraction is frequently exploited in the reprocessing of spent nuclear fuel (e.g., PUREX process) and treatment of radioactive waste. Several extraction reagents, such as tri-iso-octylamine (TiOA) [27,38], tri-butylphosphate (TBP) [29,39] and cyclohexanone [40], have been applied for the separation of technetium from other interferences and matrix components. Detailed information about the application of these extraction reagents have been presented in **Paper I**.

Solvent extraction offers a great advantage of selection among numerous extractants, whereby the selectivity can be readily modulated. However, it is deemed too labour intensive for routine analysis because several extraction cycles should be consecutively performed to separate the analyte from the bulk solution completely. In addition, a large volume of hazardous organic solvent may be used, which in turn produces organic waste which is harmful not only to the operators, but also to the environment. Nowadays, because of the development of chromatographic techniques, especially extraction chromatography, solvent extraction has become a less common method in routine analysis of environmental samples for ^{99}Tc , although it is still applied in some cases, for example in analysis of high level nuclear waste samples.

Anion exchange chromatography

Anion exchange chromatography is one of the most frequently used separation techniques for determination of ^{99}Tc in environmental samples. Strong basic anion exchange resins, such as Dowex 1 (or Bio-Rad AG1) resin, have high affinities for TcO_4^- in a wide range of pH and therefore are commonly applied in technetium analysis of environmental samples [30,41]. TcO_4^- can be easily adsorbed by anion exchange resin in neutral or alkali media and eluted with high concentration of nitric acid (e.g., >8 mol/L HNO_3). The main advantage of the anion exchange method for separation of technetium is the possibility to pre-concentrate technetium from large volume sample, for example up to 200 L of seawater. Furthermore, the removal of matrix components and most interferences is also effective. However, the decontamination for some important interfering anions such as RuO_4^- and MoO_4^{2-} are normally not sufficient, which is therefore not satisfactory for the determination of low level ^{99}Tc by measurement using mass spectrometric methods. To obtain a lower detection limit and more accurate analytical results, further separation of ^{99}Tc in the eluate from the anion exchange column is needed, which, in some cases, will prolong the analytical time and also increase the cost.

Extraction chromatography

Extraction chromatography (also called solid phase extraction chromatography) is an extraction process performed in a continuous and multi-stage manner on a packed column. In this technique, the stationary phase consists of extractants, which are immobilized on a porous support material. The inert support is normally composed of porous silica or organic polymers with particle sizes typically ranging between 50-150 μm . Extraction chromatography has the advantages of both solvent extraction and anion exchange chromatography, i.e. combining the selectivity of solvent extraction with the high separation efficiency of the chromatography method. Since commercialization of extraction chromatographic resins by Eichrom Technologies Inc. in 1990s, extraction chromatography has been widely used in radiochemical analysis of ^{99}Tc [26,42-44].

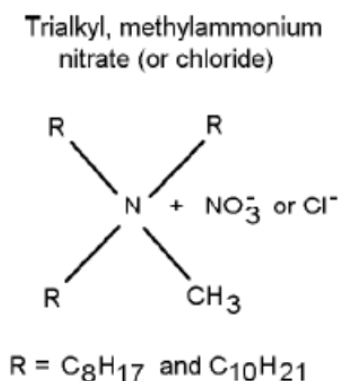


Figure 3. Structure of the TEVA Spec resin

The most commonly used extraction chromatographic resin for ^{99}Tc separation is TEVA (TEtraValent Actinides). The functional group on the TEVA resin is a trialkyl methyl ammonium salt,

also called Aliquat® 336. The structure of function group of TEVA resin is shown in Figure 3. Separation of technetium using TEVA column is based on the high affinity of TcO_4^- to TEVA resin in neutral and low acidic media (e.g., $<0.1 \text{ mol/L HNO}_3$) and the low affinity of TcO_4^- in high concentration of HNO_3 solution (e.g., $>4 \text{ mol/L HNO}_3$). Accordingly, the sample solution is usually adjusted to 0.1 mol/L HNO_3 media before loading to TEVA column, and TcO_4^- is then eluted from the resin using $\geq 8 \text{ mol/L HNO}_3$ solutions. A general procedure for separation of ^{99}Tc by extraction chromatography using the TEVA column has been shown in **Paper I (Figure 5)**.

The advantages of extraction chromatography, especially employing TEVA resin, are apparent, such as small size column, high decontamination from interferences such as molybdenum and ruthenium, high sorption capabilities to technetium, less toxic waste production, and easy adaption to automated separation setup. However, the extraction chromatographic resin is normally more expensive compared with anion exchange and solvent extraction, which to some extent limits its application for routine analysis.

1.3.4. Source preparation

Based on the detection techniques to be used, the separated ^{99}Tc has to be prepared in a suitable source before measurement. For the detection of ^{99}Tc by liquid scintillation counting (LSC) [27], the separated ^{99}Tc is normally prepared in a solution with a small volume (usually $<5 \text{ mL}$), which is mixed with scintillation cocktail for activity measurement. It is normally necessary to prepare the solution in diluted acid/alkali solution with less salt content to be able to obtain a high counting efficiency, and therefore low detection limit. When performing technetium measurement with a gas flow Geiger-Müller (GM) counter [45,46], the sample is normally prepared in solid form and the amount of final sample should be as small as possible to minimize self-absorption. Co-precipitation and electrodeposition are commonly used methods for source preparation prior to measurement of ^{99}Tc by a gas flow GM counter. In the case of mass spectrometric measurement, because of the different detection techniques, the source preparation is also different. In short, the source for accelerator mass spectrometry (AMS) is normally prepared as an oxide, and then pressed in a target holder [47]. A high purity aluminium powder with a known concentration of rhenium or niobium is added to the eluate of ^{99}Tc in a HNO_3 solution, which is then evaporated to dryness and the residue is baked to form technetium and carrier metal oxides. If the samples are measured by inductively coupled plasma mass spectrometry (ICP-MS), the final solution is usually prepared in diluted HNO_3 media (e.g., $0.3\text{-}0.6 \text{ mol/L HNO}_3$), with low salt content to be able to obtain a high detection efficiency [41].

1.3.5. ^{99}Tc measurement

For measurement of ^{99}Tc , both radiometric and mass spectrometric techniques can be utilized. These methods mainly include β counting using LSC and gas flow GM counter, neutron activation analysis (NAA), ICP-MS, AMS, thermal ionization mass spectrometry (TIMS), and resonance ionization mass spectrometry (RIMS); a comparison of different techniques for ^{99}Tc detection were presented in **Paper**

I (Table 7). Among these, β counting using gas flow GM counter or LSC, and ICP-MS are the most commonly used techniques for detection of ^{99}Tc in the environmental samples.

β counting using gas flow GM counter or LSC

Gas flow GM counter is a traditional detection technique for β emitters (such as ^{99}Tc , a pure β emitter with maximum energy of 0.294 MeV). The counting efficiency of a GM counter varies from 10% to 70% depending on the energy of the emitted β particles, thickness of the sources, and counter properties. For low level ^{99}Tc analysis in environmental samples, a low background GM counter is required. The detection limit of this technique depends on the counting efficiency, background, level, and counting time. A typical detection limit obtained by low level gas flow GM counter is in the order of several mBq, which corresponds to about 10^{-12} g of ^{99}Tc [18,45]. LSC has been accepted as a generally preferred method for counting soft β emitters such as ^{99}Tc [27]. Compared with gas flow GM counter, simple source preparation and short counting time are the main advantages of LSC. However, the higher detection limit (usually $>10^{-11}$ g of ^{99}Tc) of this technique due to higher background level constitutes a restriction for its application.

With the advantages of low cost and easy access in most of radiochemical laboratories, the β counting technique has been widely applied for the detection of ^{99}Tc in both environmental and waste samples. However, the relatively high detection limit, especially for LSC, and long counting time (usually several hours to days are needed for gas flow GM counter) are the main drawbacks of these techniques. Consequently, β counting methods are not suitable for measurement of samples in emergency situations, where analytical results should be obtained within a shorter time frame (less than one day).

Mass spectrometry using ICP-MS

ICP-MS is a rapidly growing technique which has been proven to be effective for the measurement of many long-lived radionuclides including ^{99}Tc at environmental levels [28,35,48,49]. The method has shown potential applications within environmental science, including ecosystem tracers and radio-ecological studies, and monitoring of waste discharges. Compared with β counting, ICP-MS possesses evident advantages including short measurement time (usually several minutes per sample) and relatively high sensitivity (detection limit normally in the order of 10^{-12} g for ^{99}Tc). Accordingly, this technique is a rapid, sensitive and suitable method for determination of low levels of ^{99}Tc in environmental samples.

The main challenge of this technique is the isobaric and spectrometric interferences, which will not only raise the detection limit of the method, but also reduce the reliability of the analytical results. For ^{99}Tc measurement by ICP-MS, the major problem with spectral interferences is the stable ^{99}Ru (natural abundance 12.7%) and molecular ion $^{98}\text{Mo}^1\text{H}$. Consequently, a powerful separation and purification of technetium from ruthenium and molybdenum is needed when measurement of ^{99}Tc by ICP-MS. Besides separation procedures, clean laboratory conditions, including glassware as well as

high quality chemicals are also required to avoid contamination of interferences during sample preparation.

Other detection techniques

Besides β counting and ICP-MS, ^{99}Tc can also be measured by a few other techniques such as NAA [50], AMS [51], RIMS [52], and TIMS [53]. However, because of the lack of available instruments and/or drawbacks of these techniques, they are not commonly applied for routine sample analysis. More information has been given in **Paper I**.

1.4. Species of technetium

The investigation on technetium species is primarily important to understand and evaluate its migration, toxicity and radiation risk in the environment, its accumulation in plants and animals as well as its behaviour in food chain and other ecosystem. The occurrence of different technetium species depends not only on its source and chemical properties, but also on the environmental conditions, it therefore normally exists in complicated chemical species.

1.4.1. Behaviour of different technetium species

Inorganic forms of technetium

TcO_4^- is the most important inorganic anion of technetium existing in oxidizing conditions such as in open seawater. Because of the high mobility and low interaction ability with other substances, TcO_4^- can migrate from water to soil, aquatic plants or other matrixes very easily [54]. The sorption or complexation of TcO_4^- with other substances is limited. It has been reported that the distribution coefficient (K_d) of TcO_4^- is 0 and 0.5 mL/g for mineral and organic soils, respectively [55]. The complexation of TcO_4^- with humic acid and other dissolved organic substances is only possible when the Eh value becomes negative [54]. It should be mentioned that TcO_4^- is the only chemical form of technetium known to be taken up by higher plants [56].

Under anaerobic or reductive conditions, typically in deep geological repositories, technetium mainly exists in lower oxidation states, the most common being Tc(IV), which can easily form complexes with inorganic ligands such as hydroxides, halides, carbonates, and sulphides. The behaviour of these species in the environment is usually complicated but important. In aqueous solution at low carbonic partial pressures ($P_{\text{CO}_2} < 0.1$ atm), Tc(IV) mainly exists as TcO^{2+} , $\text{TcO}(\text{OH})^+$ or $\text{TcO}(\text{OH})_2$ ($\text{TcO}_2 \cdot \text{H}_2\text{O}$) depending on the pH of solution (see Figure 1). Accordingly, $\text{TcO}_2 \cdot \text{H}_2\text{O}$ is the dominant Tc(IV) species in aqueous solution and can be co-precipitated easily using a “carrier” (e.g., $\text{Fe}(\text{OH})_2$) in neutral or alkali medium. In fact, this is the principle of the co-precipitation method to concentrate ^{99}Tc from large volume seawater samples.

Tc(IV) can also form complexes with halide ions such as the chloride ion. The chemical species of Tc(IV) in HCl media are significantly affected by the concentration of chloride ions and the acidity of the solution. In high concentrations of HCl solution, TcCl_6^{2-} is the dominant species [57]. When

decreasing the chloride ion concentration but maintaining the high acidity, a substitution of the chloride ions by water molecules occurs, and $\text{TcCl}_5(\text{H}_2\text{O})^-$ will be formed. In high concentrations of chloride ions but at low acidity, $\text{TcCl}_5(\text{OH})^{2-}$ becomes the dominant species [14]. Simultaneously decreasing the chloride ion concentration and the acidity, i.e. by dilution of HCl, TcCl_6^{2-} will transform to different intermediates and finally to $\text{TcO}_2 \cdot \text{H}_2\text{O}$ [58].

Carbonate (CO_3^{2-}) is a common ligand which widely exists in environment and can form different complexes with Tc(IV). In carbonate-enriched groundwater, the formation of highly electronegative, soluble Tc(IV) carbonate complex is a significant transport pathway for technetium [59]. A recent investigation of Tc(IV) species in bicarbonate media has shown that two species of Tc(IV) carbonate complexes $\text{Tc}(\text{OH})_2(\text{CO}_3)$ and $\text{Tc}(\text{OH})_3(\text{CO}_3)^-$ might be formed at P_{CO_2} more than 0.1 atm [60]. $\text{Tc}(\text{OH})_2(\text{CO}_3)$ is the main species of Tc(IV) in the pH range of 2-8, while $\text{Tc}(\text{OH})_3(\text{CO}_3)^-$ dominates at the pH above 8. However, Tc(IV) carbonate complexes would not dominate and significantly change the behaviour of technetium in the environment because of the low carbonic partial pressures even in the chemical conditions for deep geological formation studied for the storage of nuclear wastes (usually $P_{\text{CO}_2} < 0.1$ atm) [60].

TcS_x is another type of species of technetium, which mainly forms under sulfidic conditions and is concentrated by the sorption and/or co-precipitation with FeS or other matrixes. It was reported that TcO_4^- can be reduced to a lower oxidation state and form insoluble species TcS_2 by S^{2-} [61]. An investigation using extended X-ray absorption fine structure (EXAFS) spectrometry indicates that in reducing-agent-containing grouts, the species TcS_x appears to be identical to Tc_2S_7 , but the technetium centers in TcS_x is most likely Tc(IV) [62].

Organic form of technetium

Besides the inorganic complexes, reduced technetium can also combine with organic ligands (e.g., EDTA and humic acid) or bio-macromolecules, and finally concentrated by matrix materials. Because of the extensive distribution of organic substances in the environment, the formation of Tc-complexes with organic ligands is also various.

Organic matter like humic substances widely exist in soil and other environmental matrixes and play a key role in the migration of radionuclides in the environment. It was reported that Tc(IV)-humic complex is the dominant chemical species of technetium in deep groundwater containing humic substances, which might be a control parameter for the mobility of ^{99}Tc [63]. A recent study shows that in soils containing low quantities of natural organic matter and oxides, the presence of soluble organic ligands will likely increase the solubility and mobility of Tc(IV) species by complexation even under strictly anaerobic conditions [64]. In addition, the presence of humic materials also increases the oxidative dissolution of Tc(IV) species under oxidizing conditions by forming soluble TcO_4^- , whereas the presence of EDTA can slow this process by forming Tc(IV)-EDTA complexes.

The complexation of reduced technetium with bio-macromolecules is an important way to concentrate technetium by plants and animals and to further transport it into the food chains. For plants,

after the transport of TcO_4^- across the cell membrane, technetium will be reduced to a low oxidation state such as Tc(IV) and then combined with bio-macromolecules of the plant and fixed [56]. Different technetium complexes such as Tc-protein, Tc-cellulose and Tc-pigment have been reported in the leaves of tomato [65], spinach [66] and tree [67], although the research is still limited. For animals, to our best knowledge, there is still no more information reported about the speciation of technetium. Because of the intricate biological processes, the species of technetium in plants or animals may be expected to be more complex. To clarify the accumulation mechanism of technetium in plants, especially in aquatic plants like brown seaweeds and in marine animals such as shellfish like lobster, more work on the speciation of technetium needs to be done in the future.

1.4.2. Techniques for speciation analysis of technetium

Speciation analysis is important for the investigation of ^{99}Tc behaviour. There are mainly two techniques for the speciation analysis: computational speciation modelling and direct measurement. Computational modelling is based on thermodynamic equilibrium constants or corresponding parameters of the reactions between the components in the studied system [68]. The concentration of different species of technetium can be obtained by the computational modelling using computer codes such as PHREEQC with the conditions of known species of technetium present, the reaction constants and the total concentration of technetium. However, this method is mainly developed for simple aqueous as well as solid-liquid systems, for intricate systems like plants or animals, it is less suitable. Furthermore, there are some hypotheses in the model, which might lead to deviations compared with real environmental conditions. In addition, the lack of thermodynamic equilibrium constants for several technetium species is another limitation for its application.

Some techniques have been developed for direct speciation analysis of elements. Ultraviolet-visible (UV-visible) spectrum is a simple technique to measure different species of technetium in solution. It has been reported that the concentrations of TcO_4^- , Tc(IV), Tc(III) in HCl solution can be measured using UV-visible spectra analysis employing absorption bands at 288 nm for TcO_4^- , 512 nm for Tc(IV), and 630 nm for Tc(III) [69]. The main drawback of this technique is that the measurement is carried out at high concentrations of technetium ($>10^{-6}$ mol L^{-1} or $>10^4$ Bq/L) and in solution. EXAFS and X-ray absorption spectroscopy (XAS) are two techniques developed in the past 20 years for direct speciation analysis of elements, and have also been used for determination of different species of technetium [62,70]. These techniques are suitable for directly measuring solid samples, and the analytical results are obtained by comparing with the standards. However, due to the difficulties in preparation of suitable standards for different species of element with the same matrix as the samples, the analytical results are often semi-quantitative. Since the detection sensitivities of these techniques are still rather modest even using strong X-ray source from synchrotron, high concentrations of technetium species in the sample is still needed, which makes them difficult to use for the analysis of environmental samples without pre-concentration. Although rhenium, an analogue of technetium, has been applied for technetium speciation studies [17], the chemical behaviour of rhenium and technetium is not exactly the same, which might cause misleading conclusions regarding technetium speciation

[71]. Surface-enhanced Raman spectroscopy (SERS) is another technique which has been applied for speciation analysis of technetium in solid samples. It was reported that the primary Raman scattering band of Tc(VII) occurs at about 904 cm^{-1} , whereas Tc(IV) complexes with humic and EDTA show scattering bands at about 866 and 870 cm^{-1} respectively, a technetium concentration of $10^{-7}\text{ mol L}^{-1}$ can be measured using this technique [72]. Although the detection limit of this technique is one order of magnitude lower than that of UV-visible spectra, it is still not comparable to levels normally found in environmental samples, and thus is not suitable for investigation of technetium speciation in the environmental samples.

In the last few decades, ICP-MS has been extensively applied for the determination of low levels of ^{99}Tc in different environmental samples. However, this technique can not distinguish different species of technetium. In order to analyze technetium species, the different species of technetium have to be separated before measurement. Among various separation methods, sequential extraction is a traditional method for speciation studies of solid samples, and has been applied for the separation of different species of technetium in soil and sediments [73]. In this method, the solid sample is sequentially leached using various extracting solutions that have increasing power to release technetium from the matrix. It was reported that technetium in different forms or associated with different components of sample, including exchangeable, carbonate, reducible and oxidative fractions have been separated [74]. Technetium in fractions is then separated and further purified, and finally measured using sensitive analytical techniques, such as ICP-MS or low level gas flow GM counter. Although sequential extraction is a simple method, and widely used for fractionation of elements in solid samples, the association information, not precise information of technetium species, is obtained. In addition, many different extraction procedures including the chemical reagent, extraction order, time span, temperature, separation method of the leachate are not the same in different labs, resulting in often incomparable results. High-performance liquid chromatography (HPLC), as an effective separation technique, has also been used for the separation of different species of elements. Based on the different affinities of technetium species, retention time of technetium species on the chromatographic column is different; therefore they can be separated from each other. Maset et al. [71] investigated the association of technetium with organic matter using HPLC-ICP-MS and reported that TcO_4^- and Tc(IV)-EDTA complex can be effectively separated from the sample solution based on their different retention time: 710 s for TcO_4^- and 510 s for Tc(IV)-EDTA. By hyphenating HPLC with a sensitive detection technique, such as ICP-MS, an on-line analysis of technetium species can be implemented. However, HPLC is only suitable for solutions with a small volume ($<1\text{ mL}$); if insoluble Tc(IV) species exist, it may be adsorbed on the tubing, column or other matrixes. Furthermore, because of the difficulties in unaffected transferring all of the technetium species from a solid sample into a solution, the separation of different technetium species in solid samples using HPLC is not feasible.

In summary, techniques such as UV-visible, XAS, EXAFS and SERS are not suitable for the speciation analysis of technetium in environmental samples because of low levels of ^{99}Tc and lack of stable technetium. Mass spectrometry such as ICP-MS combined with reliable separation techniques

will be a potential method for speciation analysis. Sequential extraction is a traditional method for separating different species of technetium in solid samples with low organic matter such as soil and sediment. For biological samples like seaweeds, due to the high levels of organic matter, traditional sequential extraction techniques seems less useful, and alternative biochemical separation techniques are therefore required. For liquid samples, HPLC, especially gel chromatography is suitable for the speciation separation of technetium when present in small volumes.

1.5. Research objectives

The objective of the present work is to establish rapid and accurate analytical methods for determination of total ^{99}Tc in environmental samples (e.g., seaweed, soil and seawater), as well as speciation analysis of ^{99}Tc in seaweed. Furthermore to investigate environmental behaviour of ^{99}Tc in some specific ecosystem using the developed methods. The approaches of this thesis include:

- 1) To develop accurate analytical methods for the determination of ^{99}Tc in environmental samples using ICP-MS.
- 2) To develop an automated analytical method for determination of ^{99}Tc using the sequential injection extraction chromatographic separation approach and ICP-MS measurement.
- 3) To establish chemical separation procedures for speciation analysis of ^{99}Tc in natural seaweed.
- 4) To explore the application of ^{99}Tc as an oceanographic tracer to monitor seawater movement and coastal pollution using seaweed as a bio-indicator.

2. Experimental

2.1. Materials

^{99m}Tc tracer was obtained from 2-4 GBq commercial ^{99}Mo - ^{99m}Tc generators (Amersham, UK) and purified using alumina cartridges according to the method reported by Hou et al. [75]. A ^{99}Tc standard solution, in the form of NH_4TcO_4 with activity of 4.17 Bq/g, was supplied by Risø National Laboratory, Technical University of Denmark. Standard solutions of molybdenum, ruthenium and rhenium were obtained from CPI international (USA). Tris-HCl (purchased from AMRESCO[®], USA, purity >99.5%) buffer solution (pH \approx 7.5), and acetone (supplied by Borup Kemi I/S, Denmark, purity >95%) were used for protein and pigment fraction extraction, respectively. All other chemical reagents, including nitric acid (HNO_3), hydrochloride acid (HCl), ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium chloride (NaCl), sodium nitrate (NaNO_3), sodium carbonate (Na_2CO_3), potassium chloride (KCl), potassium disulfite ($\text{K}_2\text{S}_2\text{O}_5$), calcium chloride dihydrate ($\text{CaCl}_2\cdot 2\text{H}_2\text{O}$), iron (III) chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) used in the experiments were of analytical grade and prepared using deionized water (18.2 M Ω ·cm).

TEVA extraction chromatographic resin (particle size 100-150 μm) was purchased from TRISKEM International (Bruz, France) and applied for purification of technetium. Anion exchange chromatography (AG1- \times 4 resin, particle size 100-150 μm , Bio-Rad Laboratory, USA) was used to separate TcO_4^- from other species of technetium and concentrate rhenium from seawater samples. Before use, the resins (TEVA or AG1- \times 4) were swelled in water and transferred into an Econo-column (Bio-Rad Laboratories Inc.) and pre-treated with 8 mol/L HNO_3 to purify the resins, then the TEVA resin was washed with water and finally balanced with 0.1 mol/L HNO_3 , and the AG1- \times 4 resin was directly washed with water to neutral level.

In this study, environmental samples such as seaweed (dry and fresh), seawater, and soil were applied for the method development. Reference/certified materials including IAEA-375 (soil), IAEA-446 (seaweed), NIST-4359 (seaweed), and Danish seawater (analyzed by a conventional radiometric method) have been used for evaluation of method's reliability. More information about these samples mentioned has been given in Table 1.

Table 1. Summary of samples analyzed in this study

Sample types	Sizes for each experiment	Sampling area/location
Danish seaweed	5-10 g dry	Collected in the Klint (Kattegat, Denmark)
Danish seaweed	10-20 g fresh	Collected in Hvide Sande (west coast of Denmark) during 2011-2012
Danish soil	10-500 g dry	Collected from 12 different Danish locations in 2003
Seawater	50-200 L	Collected in the Klint (Kattegat, Denmark)
Seawater	0.5 L	Collected in Norwegian Sea in 2011
Norwegian seaweed	1 g	Collected in Hillesøy (northwest coast of Norway) during 1998-2009
IAEA-375 (soil)	10 g	Collected from Novozykov, Brjansk, Russia in 1990 (Chernobyl contaminated soil)
IAEA-446 (seaweed)	5 g	Collected from Øresund (Baltic Sea <i>Fucus</i>) in 2007
NIST-4359 (seaweed)	5 g	Collected from the western coast of Ireland and from the White Sea

2.2. Total technetium analysis

2.2.1. Sample pre-treatment

According to the sample type such as aqueous (e.g., seawater) and solid (e.g., seaweed, soil and sediment) samples, different pre-treatment procedures have been developed and applied during the sample analysis.

For solid samples (e.g., seaweed, soil and sediment), the impurity materials such as stones and roots of vegetations were carefully removed. A sufficient amount of samples was then dried at 105 °C, ground, and sieved through a 0.1 mm sieve to get a homogeneous and representative sample for analysis. After weighting to a crucible (or beaker) and spiking with ^{99m}Tc ($^{99m}\text{TcO}_4^-$ form) as a yield monitor, organic matter in the sample was decomposed by incinerating in muffle furnaces. To disperse $^{99m}\text{TcO}_4^-$ in the samples uniformly, a small amount of $\text{NH}_3\cdot\text{H}_2\text{O}$ was added and mixed with the samples, then dried on a hot plate at 100 °C before ashing. Considering the amount of organic matter in the samples, different ashing procedures were applied. Due to high amount of organic matter (normally around 80%) as well as high salt content, seaweed samples were ashed at 700 °C for 3 h to completely decompose organic matter. For soil and sediment samples, a relatively low ashing temperature, 550 °C was chosen and same ashing time was applied. The ashed samples were then digested with a solution of 3 mol/L HCl and 30% H_2O_2 (4:1 for volume ratio) on a hot plate at 70-90 °C for 1.5 h under reflux to leach technetium from ashes. During the digestion, the beaker (for soil and sediment) or crucible (for seaweed) was covered with a watch-glass to prevent evaporation of the solution. After cooling, the leachate was separated by filter through a GF/A filter paper to a centrifuge tube. The pH of the leachate was adjusted to around 1 with 6 mol/L NaOH and 0.1 g Fe^{3+} (just for seaweed, no addition of iron for soil and sediment samples) was added, then 0.5 g $\text{K}_2\text{S}_2\text{O}_5$ was added under stirring to reduce technetium and iron to Tc^{4+} and Fe^{2+} , respectively. After the color of the

solution changed to almost colorless, 6 mol/L NaOH was added to adjust the solution to pH 9-10 to co-precipitate TcO_2 with $\text{Fe}(\text{OH})_2$, then centrifuged to separate the precipitate. The separated precipitate was dissolved with 10 mL of 8 mol/L HNO_3 , 5 mL of 30% H_2O_2 was added to oxidize Tc^{4+} and Fe^{2+} to TcO_4^- and Fe^{3+} , respectively. Then 6 mol/L NaOH was added to pH 9-10 to remove iron and other transition metals as hydroxides in the precipitate. The supernatant containing TcO_4^- was transferred to a clean beaker. To reduce the loss of technetium during precipitation of hydroxides of metals due to entrapment in the precipitate, the precipitate was redissolved with 5 mL of 8 mol/L HNO_3 , and precipitation was repeated by addition of 6 mol/L NaOH to pH 9-10. After centrifuging, the supernatants were combined for chromatographic separation.

For processing large amount soil or sediment samples (e.g., >50 g soil), after ashing and leaching, a extra precipitation was applied to remove the bulk amount of iron and other elements easily precipitated from the sample matrix, then 0.1 g Fe^{3+} was added, and the same procedure mentioned above was followed.

For seawater analysis, a certain volume of sample (50-200 L) was first filtered to a container through a filter paper, and then acidified to pH 2-3 using concentrated HCl. After spiking with $^{99\text{m}}\text{Tc}$ (about 500 Bq) as a yield tracer, about 0.8 g Fe^{3+} (as FeCl_3 solution) was added, $\text{K}_2\text{S}_2\text{O}_5$ (1 g/L seawater) was used to reduce TcO_4^- and Fe^{3+} to Tc^{4+} and Fe^{2+} , respectively. After mixing by air bubbling, the pH of the sample solution was adjusted to 9-10 using 6 mol/L NaOH and technetium as TcO_2 was co-precipitated with $\text{Fe}(\text{OH})_2$ and other hydroxides (mainly $\text{Mg}(\text{OH})_2$). After gravitationally settling for 6-8 h, the supernatant was discarded and the remaining slurry was transferred to a plastic container (20-50 L). Concentrated HCl was added to dissolve the precipitate and adjust pH to 2-3, some $\text{K}_2\text{S}_2\text{O}_5$ (1 g/L) was added to remain technetium at low oxidation state of Tc^{4+} . The pH of the solution was adjusted to 8-9 using $\text{NH}_3 \cdot \text{H}_2\text{O}$ and the precipitate of TcO_2 and $\text{Fe}(\text{OH})_2$ was settled down by gravity for 3-4 h. The precipitate was dissolved with 60 mL of 3 mol/L HCl and transferred to a glass beaker; 30 mL of 30% H_2O_2 was added to oxidize Tc^{4+} and Fe^{2+} to TcO_4^- and Fe^{3+} , respectively. The sample solution was then diluted to 1 L with deionized water and 6 mol/L NaOH was added to pH 9-10 to remove Fe^{3+} as $\text{Fe}(\text{OH})_3$ precipitate. The supernatant, containing TcO_4^- , was transferred to another beaker and the pH of the solution was adjusted to 2-3 with concentrated HCl and 0.1 g Fe^{3+} (as FeCl_3 solution) and $\text{K}_2\text{S}_2\text{O}_5$ (1 g/L) was added to the solution. After stirring for 10-15 min, 6 mol/L NaOH was added to adjust pH to 9-10, the formed co-precipitate of TcO_2 with $\text{Fe}(\text{OH})_2$ was separated by centrifuging at 4000 rpm for 10 min. The precipitate was dissolved with 10 mL of 8 mol/L HNO_3 and then followed the same pre-treatment procedure as solid samples.

2.2.2. Separation of technetium using extraction chromatographic techniques

Batch sorption experiment

Extraction chromatography using TEVA resin was applied for the separation and purification of technetium before ^{99}Tc measurement by ICP-MS. A batch technique was used to investigate the sorption behaviour of technetium as well as molybdenum and ruthenium (two main interferences

of ^{99}Tc in the ICP-MS measurement) onto the TEVA resin. About 0.2 g TEVA resin was added to a 20 mL glass bottle with 10 mL of solution (HNO_3 , HCl , NaNO_3 or KCl) in different concentrations to get a final solid-to-liquid ratio of 20 g/L. A known amount of molybdenum (MoO_4^{2-} , 100 $\mu\text{g/L}$) and ruthenium (RuO_4^{2-} , 10 $\mu\text{g/L}$) as well as $^{99\text{m}}\text{TcO}_4^-$ (100 ng/L $^{99}\text{TcO}_4^-$) were added to the solution and then shaken for 6 h at room temperature. If the $^{99\text{m}}\text{Tc}$ tracer was not used, the batch experiment for technetium needed to be carried out separately to avoid the interference of molybdenum and ruthenium in the ICP-MS measurement. For the low concentration of electrolyte solution (e.g., <2 mol/L), the resin and solution was separated by centrifuging at 4000 rpm for 10 min. The resin in high concentration of electrolyte solution (e.g., >2 mol/L) was separated by filtration using a filter paper because the resin is still suspended in the solution after centrifugation and difficult to separate them. The solution (about 5 mL) was measured by a NaI γ detector to obtain the activities of $^{99\text{m}}\text{Tc}$, and by ICP-MS for molybdenum and ruthenium or ^{99}Tc after a suitable dilution using 0.5 mol/L HNO_3 . Given A_0 ($\mu\text{g/L}$ or Bq/L) as the total analytes added, and A_{eq} ($\mu\text{g/L}$ or Bq/L) as the concentration of analytes in solution after sorption, the distribution coefficient (K_d , mL/g) of these elements onto TEVA resin in different conditions can be calculated by:

$$K_d = \frac{(A_0 - A_{eq})}{A_{eq}} \cdot \frac{V}{m} \quad (1)$$

where V (mL) is the volume of aqueous solution and m (g) the mass of TEVA resin.

Separation and purification of technetium

To remove ruthenium and molybdenum from samples, two small TEVA columns (1.5 mL TEVA resin for each) were applied in the present work. Before extraction chromatographic separation of technetium, the valence of ruthenium was reduced to low oxidation state using 30% H_2O_2 in alkali media. After that, the sample solution was heated on a hot plate at 100°C to remove extra H_2O_2 and adjusted to 0.1 HNO_3 media with 8 mol/L HNO_3 . The prepared sample solution was loaded onto the first TEVA column with flow rate of 1.0-1.2 mL/min, then 40 mL of 1 mol/L HNO_3 was used to wash the column and TcO_4^- on the resin was eluted by 10 mL of 8 mol/L HNO_3 (same flow rate as the loading step). The pH of the eluate was then adjusted to around 1 with 6 mol/L NaOH and loaded onto the second TEVA column, and the procedure from the first column was repeated. Figure 4 shows the separation procedure of technetium using two TEVA columns.

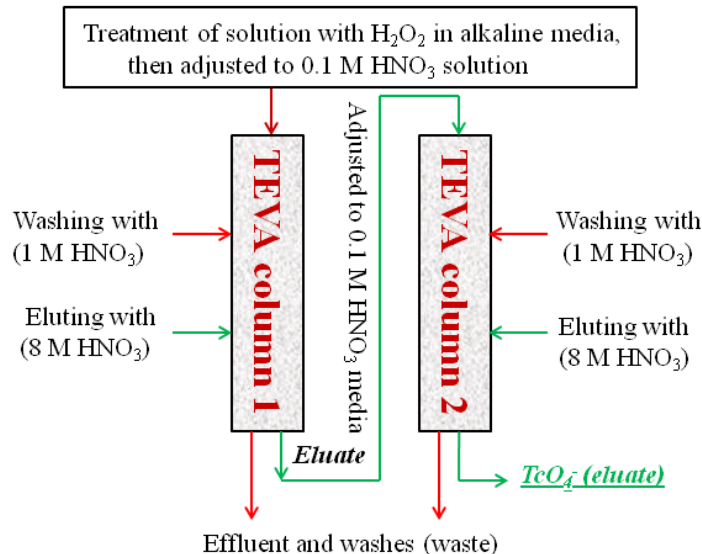


Figure 4. Schematic diagram of separation procedure for ^{99}Tc by extraction chromatography using TEVA resin (1.5 mL for each column, particle size 100-150 μm)

Automated separation system

The configurations of the sequential injection (SI) manifolds utilized in this work for automated separation of technetium consists of an FIALab-3500B SI system (FIALab Instruments, Bellevue, WA) furnished with a syringe pump (SP, Cervo, Sunnyvale, CA, 25 mL capacity), a holding coil (HC), an internal 6-ports multiposition selection valve (SV-1), four external 10-ports multiposition selection valves (SV-2, SV-3, SV-4 and SV-5), and two separation columns (SC-1 and SC-2). All the outlets of the internal selection valve (SV-1) are connected through PEEK ferrules and fitting with rigid PTFE tubing (2.4 mm i.d./3.2 mm o.d.) and all the outlets of the external selection valves (SV-2 to SV-5) are connected through PEEK ferrules and fittings with rigid PTFE tubing of smaller diameter (0.8 mm i.d./31.6 mm o.d.). The SI-system was fully automatically controlled with the aid of the user-friendly FIALab associated software. A schematic illustration of the SI-system is shown in Figure 5. The main stages of the automated separation system for technetium using extraction chromatography is as following: (i) rinsing of the holding coil with 50 mL deionized water and washing the sample inlet and outlet tubing with 0.1 mol/L HNO_3 at a flow rate of 5 mL/min; (ii) loading the sample solution (40-60 mL in 0.1 mol/L HNO_3 media) into the first TEVA column at 1.0 mL/min; (iii) washing the column with 40 mL of 1 mol/L HNO_3 at 1.0 mL/min; (iv) eluting technetium from the column with 10 mL of 8 mol/L HNO_3 at 1.0 mL/min, the eluate is directly collected in a vial in which NaOH solution was pre-filled to obtain a final solution in 0.1 mol/L HNO_3 , this solution was mixed through aspiration and injection of the solution using the syringe pump; (v) loading the obtained solution onto the second

TEVA column at 1.0 mL/min; (vi) washing the column with 40 mL of 1 mol/L HNO₃ at 1.0 mL/min; (vii) eluting technetium from the column with 10 mL of 8 mol/L HNO₃ at 1.0 mL/min.

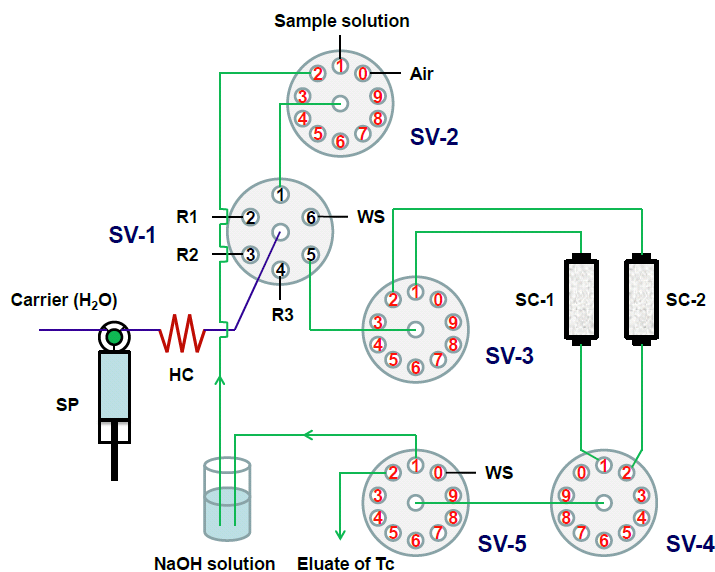


Figure 5. Schematic diagram of the sequential injection system for separation of ⁹⁹Tc from the sample matrix.

2.2.3. Source preparation

The eluate obtained from the second TEVA column was collected in a small glass beaker and evaporated to dryness at 70-90 °C on a hot plate. The residue was dissolved with 0.5 mol/L HNO₃ and transferred to a 10 mL plastic tube. A certain amount of ¹¹⁵In(III) was added to make a final concentration of 1.0 µg/L for ¹¹⁵In(III) which will be used as an internal standard for ICP-MS measurement of ⁹⁹Tc, and the final solution was diluted to 5 mL with 0.5 mol/L HNO₃.

2.2.4. Measurement

The chemical yield of technetium during the analytical procedure was monitored by measuring the activity of ^{99m}Tc (a γ emitter with γ-ray energy of 140.5 keV) using a NaI γ detector. Considering the decay of ^{99m}Tc during measurement, the ^{99m}Tc standard solution and samples were measured in each batch and measured data were correlated for radioactive decay.

The concentration of target analytes including ⁹⁹Tc, and interfering nuclides (e.g., molybdenum and ruthenium) were measured by an ICP-MS system (X Series II, Thermo Fisher Scientific, Waltham, MA), equipped with an Xs-skimmer cone and a concentric nebulizer under hot plasma conditions. A series of ⁹⁹Tc standard solutions were prepared in 0.5 mol/L HNO₃ containing 1.0 µg/L ¹¹⁵In(III) to calibrate the instrument. No carry-over (memory effect) was observed for consecutive analysis of samples differing in ⁹⁹Tc concentration up to three orders of magnitude. A linear regression line was obtained over the concentration range of 0.1 to 200 ng/L for ⁹⁹Tc. Prior to sample measurement, the ICP-MS instrument was optimized using a ⁹⁹Tc standard solution (0.1 µg/L) with a response for ⁹⁹Tc

ranged from 1×10^5 to 3×10^5 counts/s per $\mu\text{g/L}$. The typical operational conditions of the instrument for ^{99}Tc measurement are listed in Table 2.

Table 2. Typical operation conditions of ICP-MS for the measurement of technetium and rhenium

Forward power (W)	1020					
Gas flow rate (L/min)						
Coolant	13.3					
Auxiliary	1.09					
Nebulizer	0.98					
Operation pressures (mbar)						
Expansion	1.6-2.1					
Analysis	4.2×10^{-7}					
Sample uptake rate (mL/min)	0.3					
Number of replicate runs	3					
Time resolved data acquisition						
Isotopes	^{98}Mo	^{99}Tc	^{101}Ru	^{102}Ru	^{185}Re	^{187}Re
Sweeps	300	300	300	300	300	300
Dwell time (ms)	10	10	10	10	10	10
Channels per mass	1	1	1	1	1	1

2.3. Speciation analysis of ^{99}Tc

2.3.1. Chemical separation of technetium speciation in natural seaweed

To avoid the change of technetium species during drying process, fresh seaweed was used throughout in the present work. The samples were washed with seawater at the sampling location to remove the mud, sand and attached particles. They then were put onto clean plastic bags, transferred to the laboratory and preserved at $-20\text{ }^{\circ}\text{C}$. Prior to analysis, the samples were defrosted at room temperature, smashed by a grinder, and then some of them were taken for the speciation analysis of ^{99}Tc while others were dried at $60\text{ }^{\circ}\text{C}$ for total ^{99}Tc analysis.

Different species of technetium in natural seaweed were obtained using biochemical separation methods. The operational procedure is shown in Figure 6. The prepared sample (10-20 g fresh weight) was first leached 3 times with 50 mL acetone (3 h for the first time and 1 h for the second and third time, the same leaching schemes were applied in the following stages) at room temperature. After centrifuging, the supernatants were combined and distilled to remove acetone and the remaining substance is mainly pigment. The residue after acetone leaching and centrifugation was then further leached with 50 mL tris-HCl buffer solution ($\text{pH} \approx 7.5$, containing 1% CaCl_2) for 3 times at room temperature to extract water-soluble technetium. After removal of the residue, the water-soluble protein in the leachate was separated by precipitation via addition of $(\text{NH}_4)_2\text{SO}_4$ till 95% saturation, and centrifuged. The supernatant after removal of protein was then directly loaded onto an anion exchange column (AG1- $\times 4$ resin, 7 mL) to separate TcO_4^- from other water-soluble technetium species in the leachate. After washing the column with 40 mL of 1 mol/L HNO_3 , 70 mL of 8 mol/L HNO_3 was used to elute TcO_4^- from the column. The residue (after leaching with tris-HCl buffer solution) was then

leached 3 times with 50 mL of 0.2 mol/L HCl at 60 °C, and then centrifuged to obtain the acid-soluble fraction of technetium. After that, 50 mL of 0.3 mol/L Na₂CO₃ was applied to leach the residue (same leaching procedure as for the 0.2 mol/L HCl) to obtain algin (the main composition of seaweed) through the formation of soluble sodium alginate. At last, the residue was leached 3 times with 50 mL of 0.2 mol/L NaOH at 60 °C, and centrifuged. The supernatant was combined with the solution obtained after removing alginic acid precipitate to obtain alkali-soluble technetium fraction, and the final residue is mainly cellulose.

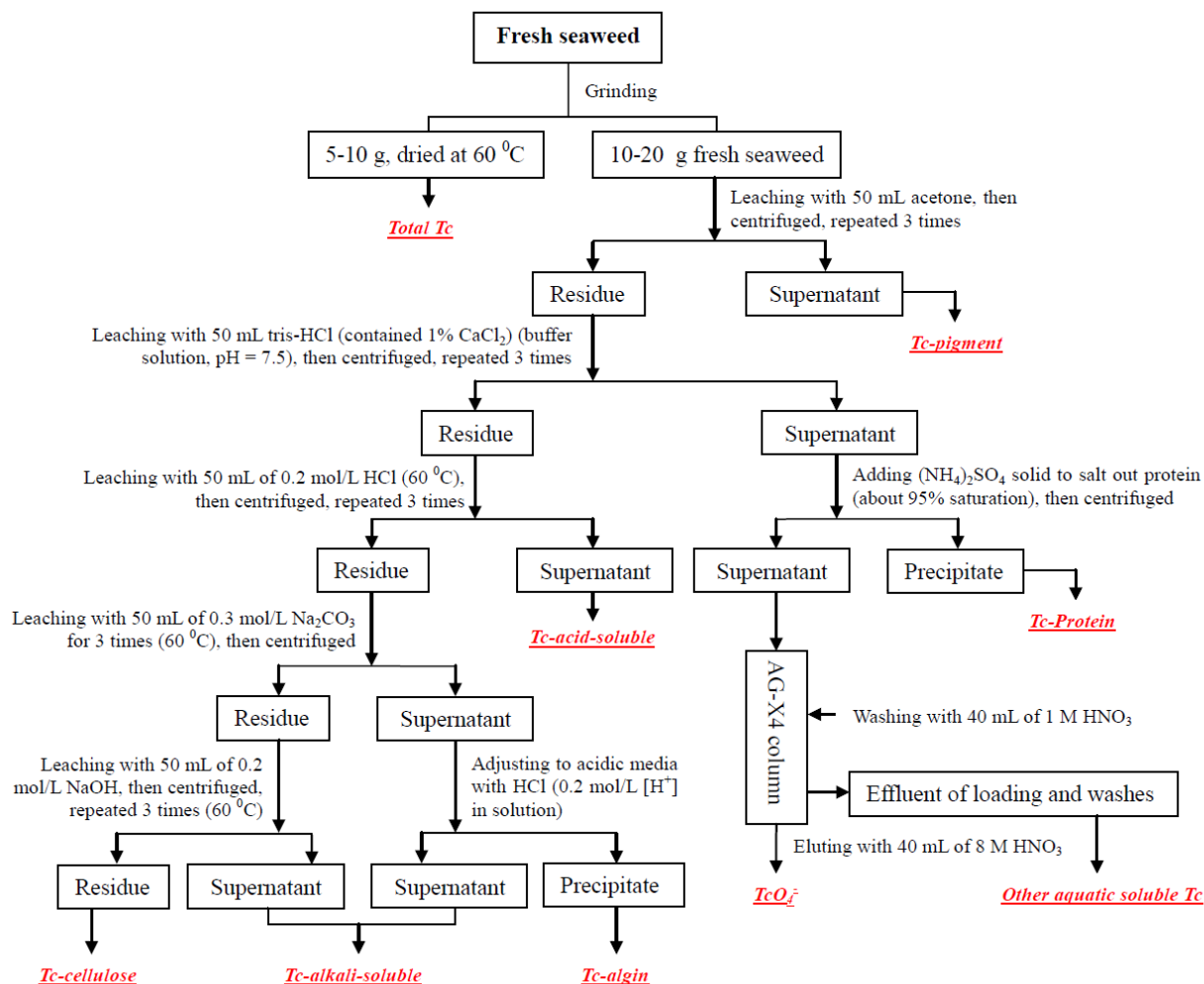


Figure 6. Diagram of separation procedure for speciation analysis of technetium in natural seaweed

2.3.2. Sample preparation and measurement

For measurement of ⁹⁹Tc in the different species separated in the above procedure, the technetium contained compounds need to be decomposed to release inorganic technetium for further separation from the matrix components and purified from interferences prior to measurement using ICP-MS. For

solid fractions such as Tc-protein, Tc-pigment, Tc-algin and Tc-cellulose, the separated fractions were dried, and analyzed with the same method as for total ^{99}Tc analysis in solid samples. To avoid the loss of technetium in these samples during dry ashing, some amount of NaCl powder was added and the sample was pre-treated with a diluted NaOH solution (e.g., $<0.01\text{ mol/L}$) and then dried before ashing.

For aqueous fractions, the eluate (8 mol/L HNO_3 with TcO_4^-) from the anion exchange column (7 mL , AG1- $\times 4$ resin) was evaporated to about 10 mL , 6 mol/L NaOH was added to pH 10-12, $30\% \text{H}_2\text{O}_2$ was then added to adjust the oxidation state of ruthenium. The same column separation procedure as for total technetium analysis was then followed. The fraction of other water-soluble technetium (effluent and washes from AG1- $\times 4$ column) was treated with $30\% \text{H}_2\text{O}_2$ to oxidize technetium to TcO_4^- , then adjusted to neutral or alkali media with 6 mol/L NaOH (pH 6-10) and loaded to an anion exchange column (7 mL , AG1- $\times 4$ resin) to concentrated technetium, TcO_4^- at last was eluted from column using 70 mL of 8 mol/L HNO_3 and further purified with the same procedure as for the TcO_4^- fraction mentioned above. For acid-soluble and alkali-soluble fractions, $30\% \text{H}_2\text{O}_2$ was added to decompose organic matters in acidic media to release technetium to solution as TcO_4^- . After removal of excess H_2O_2 by heating, 0.1 g Fe^{3+} (as FeCl_3 solution) was added. TcO_4^- was reduced by $\text{K}_2\text{S}_2\text{O}_5$ and co-precipitated with $\text{Fe}(\text{OH})_2$, then followed the same column separation and purification procedures as solid samples mentioned above. $^{99\text{m}}\text{Tc}$ was used to monitor the chemical yield of technetium, and the samples were finally measured by ICP-MS with the same operational conditions as for total technetium analysis.

2.4. Rhenium analysis

The concentrations of rhenium in seaweed and seawater samples were also determined in this work. For seaweed samples, after dry ashing, leaching with 3 mol/L HCl , and filtering, about 0.1 mL of filtrate was taken and diluted to 5 mL using 0.5 mol/L HNO_3 ($1.0\text{ }\mu\text{g/L}$ of ^{115}In contained) for measurement of rhenium by counting of the ^{187}Re isotope using ICP-MS. For seawater samples, anion exchange chromatography (AG1- $\times 4$ resin) was used to pre-concentrate and separate rhenium from the sample matrix. The eluate of 8 mol/L HNO_3 was evaporated to near dryness and prepared in 0.5 mol/L HNO_3 for measurement. A standard addition method was applied for analytical quality control. Operation conditions of ICP-MS for the measurement of rhenium are listed in Table 2.

3. Results and discussion

Determination of technetium and its speciation is a key issue for understanding the behaviour of ^{99}Tc in the ecosystem. In this thesis, analytical methods for rapid and accurate determination of total ^{99}Tc in environmental samples (e.g., seaweed, soil, and seawater), as well as speciation analysis of ^{99}Tc in seaweeds were established. The application of ^{99}Tc as an oceanographic tracer to investigate seawater movement and coastal pollution using seaweed as a bio-indicator was also investigated. The crucial experimental parameters as well as the main results are summarized and discussed in the following sections.

3.1. Stability of technetium

Because of its special physicochemical property, the stability of technetium is a very critical issue for recovery of technetium during the sample analysis. A serious loss of technetium might happen and cause a poor chemical yield and a difficulty in accurate determination of ^{99}Tc . In the present work, the stability of technetium during dry ashing of solid samples and evaporation of sample solution was comprehensively investigated.

3.1.1. Loss of technetium during sample solution evaporation

Evaporation is an often used method to reduce the sample volume and remove excessive amount of acids from the sample solution. Due to the high volatility of Tc_2O_7 (melting point of $119.5\text{ }^{\circ}\text{C}$), the loss of technetium might occur during evaporation, especially at high temperature (e.g., $>150\text{ }^{\circ}\text{C}$). To clarify parameters affecting the stability of technetium in sample solution during heating, different evaporation conditions were investigated (see details in **Paper II**). The results indicate that temperature and solution composition are the key factors determining the volatility of technetium during evaporation.

In acidic media, especially at high concentration of acid such as 8 mol/L HNO_3 solution, HTcO_4 is easily formed and can be converted to Tc_2O_7 by dehydrolysis when the solution is evaporated to dryness. In this case, the evaporation temperature should be lower (e.g., $<100\text{ }^{\circ}\text{C}$), otherwise loss of technetium will occur (Figure 7). It should be mentioned that technetium is very unstable in HCl media during evaporation, and almost all of technetium was lost during the evaporation of the sample solution (6 mol/L HCl media) to dryness at temperatures $>100\text{ }^{\circ}\text{C}$ (**Paper II**). Besides the formation of Tc_2O_7 , some other volatile species might be formed between technetium and Cl^- in HCl media. It is interesting that the addition of salt (e.g., KCl) in acidic solution can significantly reduce the loss of technetium in the evaporation process even in the HCl media. This might be explained by that technetium can attach to or be enwrapped in the formed salt crystals when the solution evaporates to dryness, isolating technetium from the high temperature bottom of the beaker, which consequently reduces the temperature directly surrounding the technetium. In addition, the formation of less volatile KTcO_4 (melts at $540\text{ }^{\circ}\text{C}$ and sublimes without decomposition at about $1027\text{ }^{\circ}\text{C}$ [2]) might be another reason.

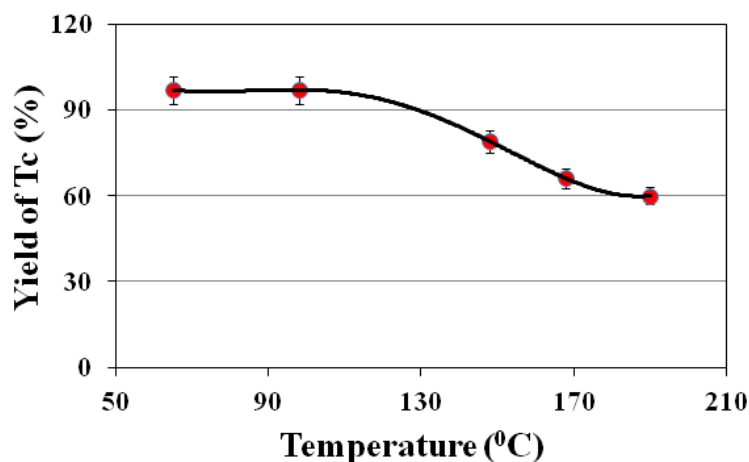


Figure 7. Effect of temperature on the loss of technetium during sample solution evaporation. A solution 10 mL of 8 mol/L HNO_3 containing $^{99\text{m}}\text{TcO}_4^-$ in a glass beaker was evaporated to dryness on a hot plate at different temperature. The experimental results are presented as the average \pm 2SD of three replicates.

Compared with acidic media, technetium in alkali solution is relative stable during evaporation [32], and no significant loss of technetium was observed in $\text{NH}_3\cdot\text{H}_2\text{O}$ solutions even with the evaporation temperature of up to 150 $^\circ\text{C}$ to dryness (Table 3). The results are in good agreement with the values obtained in different concentrations of NaOH (0.1 and 0.01 mol/L) with the same evaporation conditions as for $\text{NH}_3\cdot\text{H}_2\text{O}$ solutions. However, when the temperature increased (e.g., 200 $^\circ\text{C}$), a significant loss of technetium was observed for $\text{NH}_3\cdot\text{H}_2\text{O}$ solutions, but not in NaOH solution. This might be explained by that when the solution is evaporated to dryness, all excessive $\text{NH}_3\cdot\text{H}_2\text{O}$ is removed, and at high temperature technetium could be converted to Tc_2O_7 to some extent and lost. Compared with $\text{NH}_3\cdot\text{H}_2\text{O}$ (~71%), higher yield of technetium (>98%) was obtained in NaOH media when the solution was evaporated to dryness at 200 $^\circ\text{C}$ (Table 3), indicating that the existence of OH^- in solution can effectively suppress the formation of Tc_2O_7 , which in turn reduces the loss of technetium during sample solution evaporation. In addition, formation of solid phase NaOH when the solution was evaporated to dryness can act as other salts (e.g., KCl or NaCl) to enwrap technetium in the crystal and reduce the direct contact of technetium with high temperature beaker bottom, then reduce the loss of technetium during heating.

Table 3. Stability of technetium during evaporation of sample solution in alkali media at different temperature^{*}

Solution media	Yields of technetium at different temperature on a hot plate (%)		
	100 ± 2 °C	150 ± 2 °C	200 ± 2 °C
25% NH ₃ ·H ₂ O	97.0 ± 2.1	94.6 ± 1.9	71.1 ± 2.6
0.1 mol/L NaOH	98.0 ± 1.8	99.1 ± 1.5	101.3 ± 1.2
0.01 mol/L NaOH	98.4 ± 2.6	97.8 ± 2.3	98.9 ± 2.7

^{*}The sample solutions were evaporated to dryness and then prepared for measurement. The results are presented as the average ± 2SD of the three replicates.

It is interesting that no significant loss of technetium was observed if the solution was not evaporated to complete dryness even in HCl media. This indicates that the loss of technetium mainly happens after the solution is evaporated to dryness. This phenomenon might be explained by that HTcO₄ or a complex of technetium with Cl⁻ in HCl media is relatively stable in solution. When the solution is removed, the formed HTcO₄ or a complex of technetium with Cl⁻ is decomposed and forms more volatile species of technetium such as Tc₂O₇. In addition, the temperature applied to technetium species also increased when evaporated to dryness compared with the solution, which enhances the loss of the formed technetium species.

In summary, to avoid significant loss of technetium during sample solution evaporation, it is recommended that the sample solution is better to be adjusted to alkali media with NaOH before evaporation. For HNO₃ media, technetium solutions should be evaporated at lower temperature (e.g., <100 °C) if the solution needs to be evaporated to dryness or remain some solution left (e.g., 0.5 mL) at higher temperature (e.g., >100 °C). For HCl media, especially with high concentrations of HCl, the sample solution should not be evaporated to complete dryness even at low temperature (e.g., <100 °C).

3.1.2. Loss of technetium during solid sample dry ashing

Dry ashing is a simple and effective method to decompose organic matter in solid samples to be able to extract technetium from the residue using acid solution. However, technetium might be lost from the sample through formation of volatile technetium species such as Tc₂O₇ during heating at high temperature [30]. On the contrary, organic matter cannot be completely incinerated at low temperature (e.g., <500 °C), which may otherwise lead to complications in the subsequent chemical processing and cause a poor chemical yield of technetium [26]. In the present work, possible factors influencing the stability of technetium during dry ashing process were investigated to establish rapid and reliable pre-treatment methods for solid sample analysis.

For biological samples such as seaweed, because of the high amount of organic matter (>80%) and salt content, the ashing can be carried out at relatively high temperature [26]. A low chemical yield is often obtained if seaweed sample is not ashed completely (some black carbon remains). This is because that most of technetium might associate with organic compounds in the seaweed samples, which cannot be completely released from the undecomposed samples. Various parameters including ashing temperature, time as well as pre-treatment methods before ashing were investigated. The results (see **Table 2** in **Paper II**) show that dry ashing at 700 °C for 3 h is an optimal condition to completely

decompose organic matter in seaweed and to avoid the significant loss of technetium during heating. The pre-treatment of sample by $\text{NH}_3 \cdot \text{H}_2\text{O}$ before ashing is not effective to improve the stability of technetium, but it is helpful to make the sample fluffy and therefore easier to be completely ashed. However, the addition of HCl in the sample before ashing shows a negative effect on the stability of technetium. This might be attributed to the formation of volatile species of technetium in HCl media at high temperature.

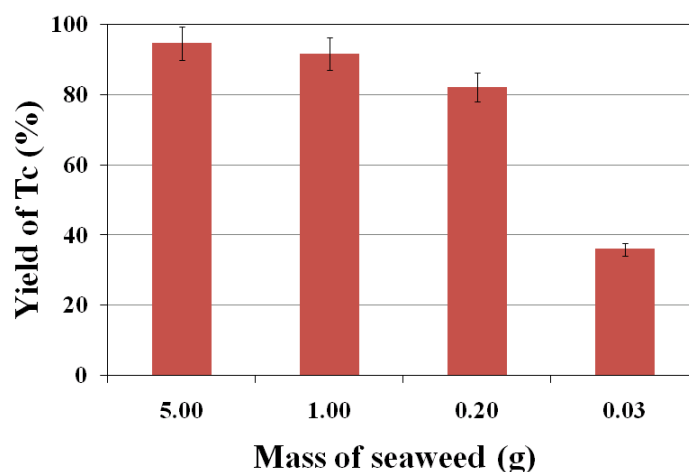


Figure 8. Effect of sample size on the loss of technetium during dry ashing of seaweed at 700 °C for 3 h. The results are presented as the average \pm 2SD of three replicates.

Due to the high accumulation of technetium in brown seaweed, the amount of seaweed sample usually required for ^{99}Tc determination is relatively small, especially for samples collected near the reprocessing plants (e.g., Sellafield and La Hague), where sample sizes far less than 1 g (dry weight) is sufficient. Our preliminary experiment shows that the loss of technetium happened when the amount of seaweed is less than 1 g, especially when the salt content in the seaweed is lower (e.g., seaweed collected in low salinity water such as the Baltic Sea). By investigating the effect of seaweed sample mass on the stability of technetium during dry ashing, it was observed that the loss of technetium increased with the decrease of sample size, and a significant loss of technetium was observed when the seaweed sample is less than 1 g (Figure 8). As mentioned above, technetium might be attached to or enwrapped in matrix component during heating, if the sample size becomes smaller, the residue after ashing is also less, which in turn reduces the possibility of technetium attached to or enwrapped in matrix component and thus causes loss of technetium. Further investigation on the pre-treatment of seaweed samples (<1 g) with different methods before dry ashing shows that the addition of salt such as NaCl (about 0.5 g) and diluted NaOH solution in the sample before ashing can significantly reduce the loss of technetium, which might be explained by that technetium can attach to or be enwrapped in the formed salt crystals or form more stable technetium species in alkali media during ashing at high temperature.

Because of the low content of organic matter, soil and sediment samples are usually ashed at relatively low temperature (e.g., $<700^{\circ}\text{C}$) [18]. Our experimental results show that organic matter in soil sample can be completely decomposed at 550°C for 3 h. The loss of technetium increases with increasing temperature and only 30% of technetium was recovered when ashing temperature was increased to 700°C and remained for 3 h (10 g soil, dry weight) (Figure 9). Compared with seaweed, the loss of technetium is obvious in soil sample at high temperature. This can be explained that the composition of these two types of samples is different. Possibly unstable species of technetium might easily be formed when soil samples are ashed. Pre-treatment experiments show that the stability of technetium can be significantly improved if the soil sample is pre-treated with NaOH solution before ashing (Figure 10). Compared with $\text{NH}_3\cdot\text{H}_2\text{O}$ ($<30\%$), a higher yield of technetium ($>70\%$) was obtained when treated with diluted NaOH ($<0.01\text{ mol/L}$), this can be explained by that NaOH is much more stable than $\text{NH}_3\cdot\text{H}_2\text{O}$ during heating, an alkali atmosphere is kept during the whole ashing process which suppresses the formation of unstable species of technetium such as Tc_2O_7 in NaOH media. It is interesting that the addition of some NaCl (or KCl) in soil sample pretreated with NaOH solution before ashing can effectively improve the stability of technetium even at such a high temperature as 700°C (Figure 10), indicating that the level of salt (e.g., NaCl) in a sample might be an important factor for the loss of technetium. A suggested explanation to this may be that a relatively stable technetium complex might be formed between technetium and Cl^- in alkali media when NaCl or KCl added in the sample during ashing.

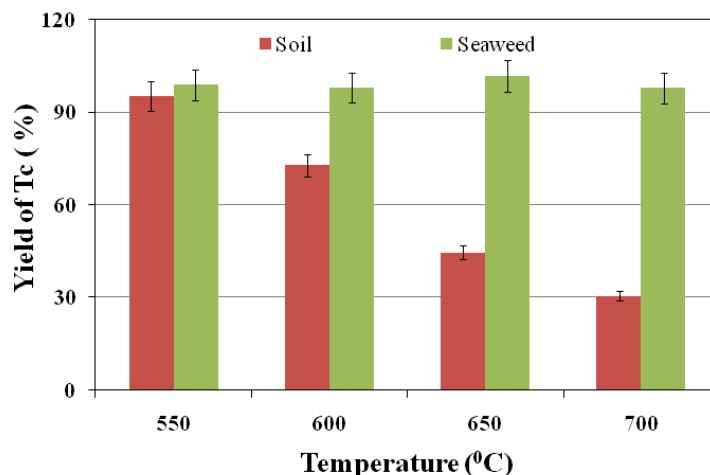


Figure 9. Effect of ashing temperature and sample type on the loss of technetium during dry ashing of 10 g samples pre-treated with $\text{NH}_3\cdot\text{H}_2\text{O}$ and ashed for 3 h. The results are presented as the average \pm 2SD of three replicates.

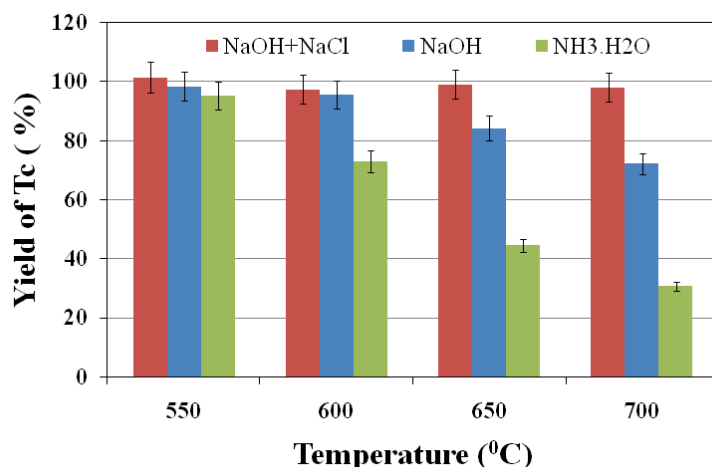


Figure 10. Effect of pre-treatment methods and temperature on the loss of technetium during dry ashing of 10 g soil samples for 3 h. The results are presented as the average \pm 2SD of three replicates.

Based on the above experiment, the optimal procedures for dry ashing of environmental solid samples are obtained: (i) for biological samples such as seaweed (≥ 1 g dry weight), the sample can be directly ashed at 700 °C for 3 h; (ii) for small size of seaweed samples (< 1 g dry weight), some KCl or NaCl (about 0.5 g) needs to be added and pre-treated with a diluted NaOH solution (e.g., 0.01 mol/L), and then ashed at 700 °C for 3 h; (iii) for soil samples, the dry ashing can be carried out at 550 °C for 3 h without any pre-treatment. If soil sample has to be ashed at a higher temperature (e.g., 700 °C), the addition of KCl or NaCl and pre-treatment of sample with a diluted NaOH solution are needed.

3.2. Separation of technetium from sample matrix and main interferences

The method adopted for the separation of ^{99}Tc should be able not only to give a good decontamination from interference but also to provide a high chemical yield of ^{99}Tc . In this work, a co-precipitation method was optimized for rapid pre-concentration of ^{99}Tc in large volume seawater samples. Extraction chromatographic technique using TEVA column was applied for purification of technetium prior to ICP-MS measurement.

3.2.1. Co-precipitation of technetium from large volume seawater

Co-precipitation using $\text{Fe}(\text{OH})_2$ is an effective and simple method to preconcentrate technetium from water samples, especially suitable for pre-treatment of water samples in the field, which avoids the problem of transporting large volume water samples back to the home laboratory [5].

The amount of iron added as a carrier is critical to the yield of technetium in the following steps. Our experimental results indicate that most of technetium ($> 85\%$) can be co-precipitated by $\text{Fe}(\text{OH})_2$ with an iron amount of 0.8 g when processing 50 L seawater samples (**Paper III, Figure 3**). To avoid the formation of a bulky iron hydroxide precipitate, which will cause problems in the following separation stages such as difficulties in dissolving the precipitate with a small volume of acid, the same amount of

iron (0.8 g) was also used to enrich technetium from as large a sample as 200 L seawater based on a two-step co-precipitation protocol. That is, after iron and $\text{K}_2\text{S}_2\text{O}_5$ (1 g/L) are added, the pH of the sample solution is first adjusted to 9-10 using 6 mol/L NaOH to form $\text{Fe}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ precipitates in which technetium is co-precipitated. After removal of the supernatant, the precipitate was dissolved with acid and $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added to the solution to form only a $\text{Fe}(\text{OH})_2$ precipitate (technetium is co-precipitated) for further preconcentration of technetium. Accordingly, a yield of technetium (>85%) was obtained during the co-precipitation step for up to 200 L seawater sample.

3.2.2. Technetium separation and purification using extraction chromatography

Extraction chromatography using the TEVA resin has been proved to be an efficient method to separate technetium from other interferences [25,29,36]. A comprehensive investigation on the sorption and elution behaviour of technetium onto TEVA resin and decontamination from ruthenium and molybdenum using TEVA column was carried out in the present work.

Distribution coefficients of technetium, ruthenium, and molybdenum onto TEVA resin

Sorption of TcO_4^- , MoO_4^{2-} and RuO_4^{2-} onto TEVA resin in different concentrations of HNO_3 was investigated by batch experiments. The results (see **Figure 2** in **Paper II**) show that the distribution coefficient (K_d) of TcO_4^- and MoO_4^{2-} onto TEVA resin decrease with the increase of HNO_3 concentration. Compared with MoO_4^{2-} , high affinity of TcO_4^- onto TEVA resin was observed at low concentration of HNO_3 (e.g., <1 mol/L). To remove the molybdenum but remain technetium on the column, a loading sample solution in 0.1 mol/L HNO_3 media and a washing solution of 1 mol/L HNO_3 were selected. Although a relatively low K_d of RuO_4^{2-} onto the TEVA resin was observed, because the affinity of RuO_4^{2-} onto TEVA resin is insensitive with the variation of HNO_3 concentration, the adsorbed ruthenium is not easily removed from the TEVA column by washing with HNO_3 in a higher concentration (e.g., 1 mol/L).

Valence adjustment of ruthenium

The chemical property of ruthenium is relatively complex with oxidation states varying from +1 to +7 under different conditions. Among them, RuO_4^{2-} and RuO_4^- are the two major inorganic anions existing in the aqueous solutions. RuO_4^{2-} can be easily oxidized to RuO_4^- in alkali media and to RuO_4 in acidic media by strong oxidants such as NaClO [76]. On the contrary, RuO_4^- can be reduced to RuO_4^{2-} or even lower oxidation states such as Ru^{4+} under reducing conditions. Because of the similar chemical characteristics of RuO_4^- and TcO_4^- , the sufficient removal of ruthenium from technetium seems to be difficult if technetium and ruthenium are held in the $\text{TcO}_4^-/\text{RuO}_4^-$ state. Compared with technetium, ruthenium is more sensitive to redox reactions and can be reduced to a lower oxidation state by weak reducing reagent such as Cl^- [76]. Based on the middle valence of oxygen atom in H_2O_2 (between 0 and -2), H_2O_2 can be used either as an oxidant or as reducing reagent. According to the report by Chen et al. [19], RuO_4^- can be reduced to a lower oxidation state by 30% H_2O_2 in alkali media. In the present work, a valence adjustment of ruthenium using 30% H_2O_2 was investigated before TEVA column separation. The results show that the treatment of the loading solution with 30%

H₂O₂ in alkali media can significantly reduce the sorption of ruthenium onto the TEVA column (see **Table 3** in **Paper II**).

Decontamination of molybdenum and ruthenium using two TEVA columns

For measurement of ⁹⁹Tc by ICP-MS, the main challenges are the isobaric interferences at 99 amu mainly from stable ⁹⁹Ru and the molecular ion ⁹⁸Mo¹H. To obtain a low detection limit as well as reliable analytical results, efficient removal of molybdenum and ruthenium from sample solution is needed. Based on the findings above, extraction chromatography using TEVA column is applied to decontaminate molybdenum and ruthenium. Considering the effect of matrix elements on the sorption capacities of TEVA resin for TcO₄⁻, a volume of 1.5 mL resin was utilized in this work (see details in **Paper III**). Our results show that one TEVA column is not enough to sufficiently remove molybdenum and ruthenium because of the high levels of these two elements compared with technetium in most environmental samples (Figure 11). Therefore a setup of two small TEVA columns has been established in the present work. It was observed that by repeating the separation procedure on two consecutive TEVA columns, almost all of the ruthenium and most of molybdenum could be removed while technetium was still retrieved with a high chemical yield (Figure 11). Combined with the valence adjustment of ruthenium with 30% H₂O₂ and separation using two TEVA columns, decontamination factors of more than 1×10⁵ for ruthenium and 4×10⁴ for molybdenum was obtained with the chemical yield of technetium ranged from 60% to 95% for different types of environmental samples.

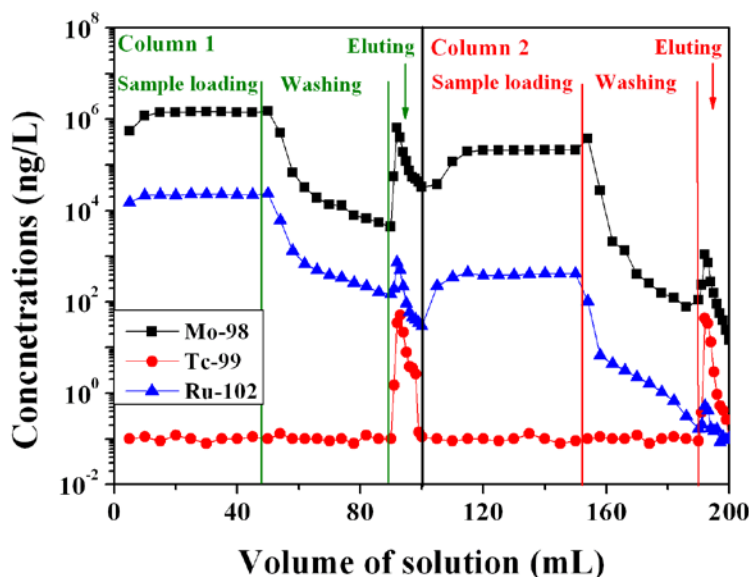


Figure 11. Sorption and elution behaviour of technetium, ruthenium, and molybdenum in extraction chromatographic separation using two small TEVA columns (1.5 mL for each). The sample solutions were

adjusted to pH ≈ 1 with 8 mol/L HNO_3 before loading; the column was washed with 40 mL of 1 mol/L HNO_3 , and the analytes were eluted with 10 mL of 8 mol/L HNO_3 .

Sorption and elution behaviour of TcO_4^- onto TEVA column

Based on the high affinity of TcO_4^- onto the TEVA resin, TEVA column has been widely applied to separate technetium from the sample matrix and interferences [26,77]. The sample solution is usually loaded onto the column in low concentration of HNO_3 media (e.g., <0.1 mol/L) and adsorbed technetium is then eluted from the column using high concentration of HNO_3 (e.g., >8 mol/L). However, the sorption and elution mechanism of TcO_4^- onto the TEVA resin is still not very clear although the ion exchange reaction has been proposed [77].

An investigation on the effect of $[\text{H}^+]$ and $[\text{NO}_3^-]$ on the sorption of TcO_4^- onto the TEVA resin was carried out in the present work. The results (Figure 12) show that the K_d value of technetium is significantly higher (about 500) in NaNO_3 solution (pH ≈ 1) compared with HNO_3 media (about 2) with the same NO_3^- concentration of 6 mol/L, which indicates that $[\text{NO}_3^-]$ is not the only factor controlling the sorption of TcO_4^- onto the TEVA resin, $[\text{H}^+]$ is another key parameter, probably the dominant factor for desorption of TcO_4^- from the TEVA column in the eluting process using a high concentration of HNO_3 . Further studies on the sorption behaviour of TcO_4^- onto TEVA resin in KCl and HCl media confirm that $[\text{H}^+]$ is the main factor affecting the sorption of TcO_4^- onto TEVA resin (Figure 12).

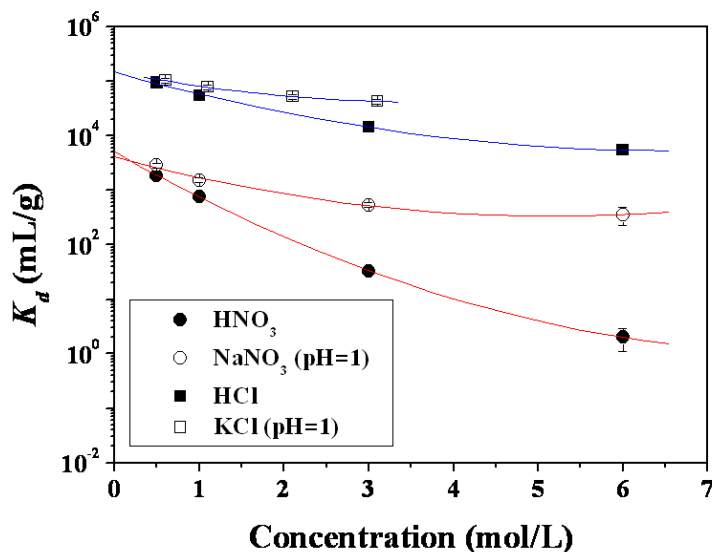


Figure 12. Effects of $[\text{H}^+]$, $[\text{NO}_3^-]$ and $[\text{Cl}^-]$ on the sorption of TcO_4^- onto the TEVA resin, obtained at room temperature following an equilibrium time of 3 h and solid-to-liquid ratio of 20 g/L. The average and 2 SD of three replicates are shown.

On the basis of these findings, the possible mechanism controlling TcO_4^- sorption onto TEVA resin at different concentrations of H^+ can be deduced. At low $[\text{H}^+]$, technetium mainly exists in the form of TcO_4^- , which shows a high affinity to the TEVA resin. With increasing $[\text{H}^+]$, the formation of the

neutral molecule HTcO_4 becomes dominated, which leads to a decreased concentration of TcO_4^- in solution, causing a low K_d value for technetium. Although the sorption of TcO_4^- onto TEVA is stronger compared with NO_3^- , the replacement of TcO_4^- from the resin by NO_3^- can occur when NO_3^- concentration is increased. In conclusion, elution of TcO_4^- from TEVA column with a high concentration of HNO_3 is based on two factors, formation of HTcO_4 and replacement of TcO_4^- by NO_3^- , of which the former is dominant.

Recommended separation procedure for technetium using two TEVA columns

According to the discussion above, after valence adjustment of ruthenium using 30% H_2O_2 in alkali media, a procedure for separation of technetium and decontamination from molybdenum and ruthenium using two small TEVA columns was established. The main steps of this procedure are as following:

- i) Pre-condition TEVA columns (1.5 mL resin for each, particle size 100-150 μm) with 20 mL concentrated HNO_3 , wash with some H_2O to lower acidity and then equilibrate with 10 mL 0.1 mol/L HNO_3 ;
- ii) Load the sample solution (0.1 mol/L HNO_3 media) to the first TEVA column at a flow rate of 1.0-1.2 mL/min;
- iii) Wash the column with 40 mL of 1 mol/L HNO_3 to remove the remained matrix elements and interferences at a flow rate of 1.0-1.2 mL/min;
- iv) Elute TcO_4^- with 10 mL of 8 mol/L HNO_3 at a flow rate of 1.0-1.2 mL/min;
- v) Adjust the pH of the eluate to 1 with 6 mol/L NaOH and load the sample solution onto the second pre-conditioned TEVA column with the same flow rate;
- vi) Follow the same steps of washing and elution as for the first column, collect the eluate from the second column for source preparation and measurement of ^{99}Tc using ICP-MS.

3.3. Application of ^{99}Tc as an oceanographic tracer

Due to the long half-life (2.13×10^5 y), high mobility and solubility (in TcO_4^- form) and a well-know input function in the environment, ^{99}Tc is a potential oceanographic tracer to monitor seawater movement and coastal pollution [6]. The investigation on the temporal and spatial variations of ^{99}Tc concentrations in seawater is thus needed. Based on the high uptake capacities of seaweed to technetium, the determination of ^{99}Tc concentration in seaweed has been considered to be an effective way to evaluate ^{99}Tc concentrations in seawater without analyzing large volumes of seawater.

The application of seaweed as a bio-indicator to estimate the concentration of ^{99}Tc in seawater is based on an assumption that the concentration factor of ^{99}Tc in specific species of seaweed is constant and does not vary with other conditions such as sampling date. To this point, a comprehensive investigation on the concentration factor of ^{99}Tc in seaweed for its temporal variation is needed. In the present work, a study on the seasonal variation of ^{99}Tc concentration in seaweed was carried out to

explore the concentration factor as well as mechanisms influencing the seasonal variation of ^{99}Tc in *Fucus vesiculosus*. In addition, as analogue of technetium, the behaviour of rhenium in seaweed was also investigated.

3.3.1. Temporal variation of ^{99}Tc concentration in seaweed

Seasonal variations of ^{99}Tc concentration with maximum value in winter and minimum value in summer in *Fucus vesiculosus* collected at Klint (Denmark) were observed (Figure 13(A)). Several factors including variation of the monthly discharge of ^{99}Tc from reprocessing plants, the biological cycle of seaweed, and environmental processes such as the dilution of ^{99}Tc in contaminated seawater by uncontaminated water, might affect the ^{99}Tc concentration in seaweed and result in a seasonal fluctuation of ^{99}Tc concentrations.

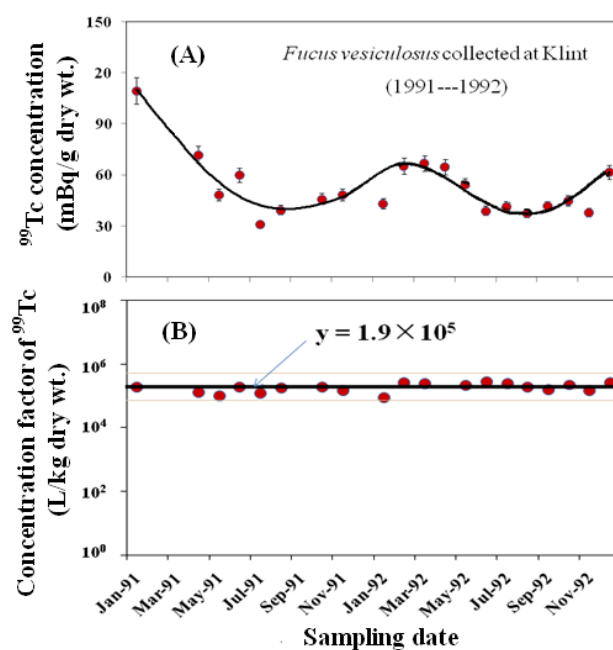


Figure 13. Seasonal variation of technetium concentration in *Fucus vesiculosus*: (A) technetium concentration; (B) concentration factors of technetium in *Fucus vesiculosus*. The results are presented as the average \pm 2SD, and the lines (in Figure (B)) show the average and upper and lower values of 2SD of all experimental data.

The increased discharges of ^{99}Tc from reprocessing plants (e.g., Sellafield and La Hague) enhance the concentration of ^{99}Tc in seawater, consequently increasing the ^{99}Tc concentration in seaweed. For the monthly seaweed samples collected at Klint, Denmark (1991-1992), the source of ^{99}Tc during that period is mainly due to releases from the La Hague reprocessing plant (see **Figure 2** in **Paper I**). Although the monthly discharge of ^{99}Tc in the years of 1989-1990 is not available (the transit time is about 2 years from La Hague to Klint [78]), according to the report by Patti et al. [79], there are no obviously seasonal variations of ^{99}Tc discharges during the period of 1985-1988 from the La Hague

reprocessing plant, which indicates that the discharges of ^{99}Tc from the reprocessing plant do not significantly contribute to the seasonal variation of ^{99}Tc concentration in seaweed.

Concentrations of elements in plants are usually related to biological processes such as plant growth [79]. Accordingly, the concentration of ^{99}Tc might decrease during its fast growth in warm conditions, causing a lower concentration of ^{99}Tc in summer. However, according to studies by Hattink et al. [80], the uptake kinetics of technetium in seaweed is relatively fast, and equilibrium of technetium between seawater and seaweed can be quickly reached. To this point, the effect of rapid growth of seaweed on the variation of technetium concentration might be limited. Of course, the distribution of technetium in seaweed is usually different, higher level in leaves and stems, and lower concentration in boluses has been observed (see **Table 1** in **Paper IV**). This is mainly attributed to the different composition in different parts of the seaweed. If the seaweed sample contains a relatively high mass fraction of boluses, the concentration of ^{99}Tc will be lower compared with the same seaweed sample but less bolus.

The Klint locates in the Kattegat (see Figure 14), where technetium contaminated water with high salinity from the North Sea is mixed with the less contaminated Baltic Sea water (low salinity). Therefore, the concentration of ^{99}Tc in seawater in this area (e.g., Klint) is significantly influenced by the water exchanges between the North Sea and the Baltic Sea [81], and a good correlation between salinity and ^{99}Tc concentration in seawater from the Kattegat has been observed [82]. In addition, the runoff of fresh water from land will also dilute the concentration of ^{99}Tc in seawater, consequently reducing the ^{99}Tc concentrations in seaweed although this effect might be not significant. Accordingly, the lower concentrations of ^{99}Tc in seaweed collected from Klint in summer compared with that in the winter time might be contributed to the dilution of ^{99}Tc concentration in seawater in summer due to higher outflow of low ^{99}Tc concentration water from the Baltic Sea to Kattegat as well as higher precipitation rate during the summer time. A similar seasonal variation of ^{99}Tc concentration in seawater collected at Klint in 1991-1992 was also observed (see **Paper IV**), which further confirms that the seasonal variation of ^{99}Tc in seaweed is attributed to the concentration of ^{99}Tc in the seawater where ^{99}Tc was uptaken.

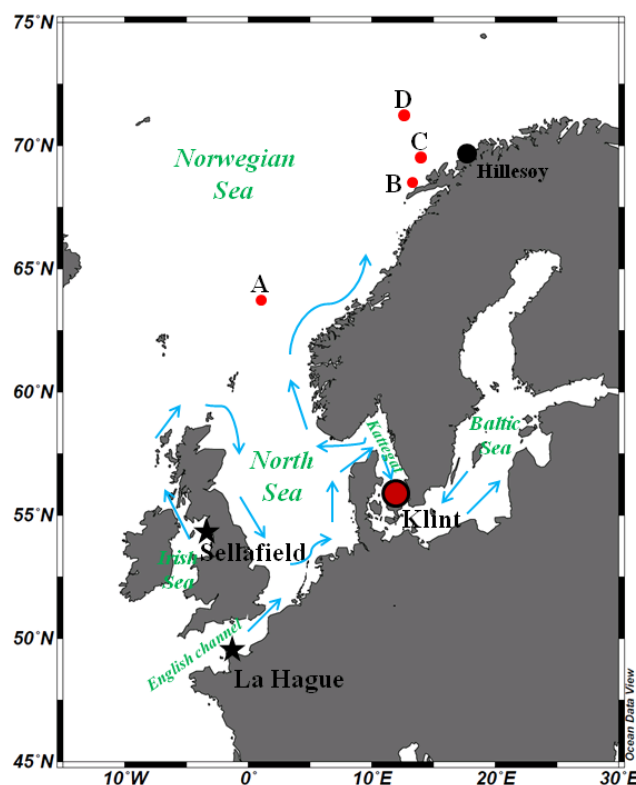


Figure 14. Sampling locations of seaweed and seawater. The major sea currents in the North Sea are also shown.

3.3. 2. Concentration factors

Concentration factor of technetium in seaweed

The accumulation capacity of a specific species of seaweed to ^{99}Tc in the marine environment can be characterized by its concentration factor (CF), which is defined as the ^{99}Tc concentration in seaweed (Bq/kg dry weight) divided by the ^{99}Tc concentration in seawater (Bq/L). By determination of ^{99}Tc concentration in seawater and seaweed samples collected monthly at the same time during 1991-1992 at Klint (Denmark), concentration factors of ^{99}Tc in *Fucus vesiculosus* were calculated. The results (Figure 13(B)) show no seasonal variation of concentration factors of ^{99}Tc although a significant seasonal cycle of ^{99}Tc concentrations in seaweed and seawater were observed. Further investigations on concentration factors of ^{99}Tc in *Fucus vesiculosus* in time series seawater and seaweed samples collected at Klint during 2000-2008 indicates that the concentration factor of a specific seaweed to technetium is an intrinsic parameter and does not vary with sampling date (see **Figure 6 in Paper IV**). The measured concentration factor of ^{99}Tc ranges from 1.3×10^5 to 2.4×10^5 L/kg with an average value and 2SD of $(1.9 \pm 0.5) \times 10^5$ L/kg. The relatively constant concentration factors of ^{99}Tc in *Fucus vesiculosus* explored in this work confirm the reliability to use seaweed as a bio-indicator for estimation of ^{99}Tc concentrations in seawater and to apply ^{99}Tc in seaweed for oceanographic tracer studies. Meanwhile, this also makes it simple to model the variation of ^{99}Tc concentrations in seaweed

based on the discharge data of ^{99}Tc from reprocessing plants, and consequently its temporal variation and spatial distribution along the coastal area.

It should be mentioned that different species of seaweed show different concentration factors. For *Fucus* species, an order of concentration factor of ^{99}Tc in *Fucus vesiculosus* > *Fucus serratus* > *Fucus spiralis* has been reported [23]. The variation of concentration factors of ^{99}Tc with different species of seaweed might be attributed to their different biological function to uptake ^{99}Tc into the plant cells and the binding mode of technetium with the corresponding components.

Concentration factor of rhenium in seaweed

As a chemical analogues of technetium, the concentration factor of *Fucus vesiculosus* for rhenium was also investigated. Time series of seaweed samples collected at Hillesøy (northwest coast of Norway) during the years of 1998-2009 were analyzed. The results (Figure 15(A)) indicate that the concentration of rhenium in *Fucus vesiculosus* is constant with a mean value of 91.4 ± 6.6 $\mu\text{g/kg}$ dry weight (2SD of uncertainty) and does not significantly vary with sampling time. The concentrations of rhenium in seawater samples collected in the Norwegian Sea (sampling locations A, B, C, and D were presented in Figure 14) and Klint (Denmark) were also determined, and a quite constant value of 4.4 ± 0.3 ng/L (2SD of uncertainty) was obtained with the regardless of sampling location and depth (Table 4). Based on these data, the concentration factor of rhenium in *Fucus vesiculosus* was calculated to be $(2.1 \pm 0.3) \times 10^4$ L/kg dry weight (Figure 15(B)). Compared with the value of ^{99}Tc , the concentration factor for rhenium is about one order of magnitude lower. This might be explained by different redox behaviour of technetium and rhenium and their uptake mechanism in seaweed. Similarly to technetium [80], the uptake of rhenium by seaweed might also be controlled by two processes: (i) transfer of ReO_4^- across the cell membrane into cell from seawater, and (ii) reduction of ReO_4^- to a low oxidation state to be able to combine with organic compounds in the cell. Compared with technetium, rhenium shows a high reduction potential, and is therefore not so easy to reduce, and accordingly rhenium compounds are less active than their technetium analogues [2]. In addition, concentrations of rhenium in seawater are more than three orders of magnitude higher compared with technetium, which might be another reason to cause a lower concentration factor of rhenium. For elements with similar chemical properties, it has been observed that elements with high concentrations in seawater normally show a lower concentration factor in seaweed [83].

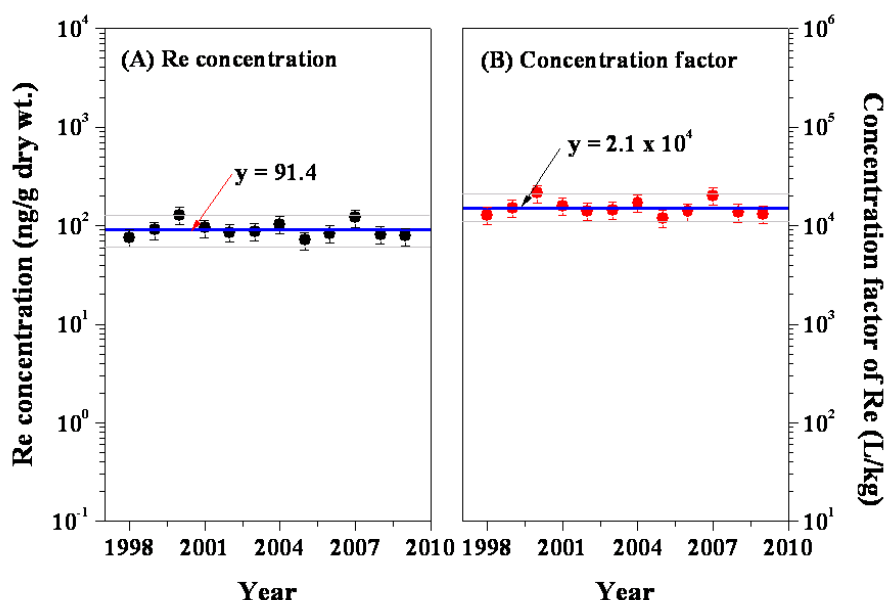


Figure 15. The uptake of rhenium by *Fucus vesiculosus*: (A) rhenium concentration in time series of seaweed; (B) concentration factors of rhenium in *Fucus vesiculosus* with temporal variation. The results are presented as the average \pm 2SD, and the lines show the average and upper and lower values of 2SD of all experimental data.

Table 4. The concentration of rhenium in seawater samples collected at Norwegian Sea and Klint

Sample locations	Depth (m)	Volume (L)	Re added (ng/L)	Re measured (ng/L) *
Kattegat (Klint)	2	0.5	0	4.6 \pm 0.3
Kattegat (Klint)	2	0.5	10	14.5 \pm 1.0
Kattegat (Klint)	2	0.5	50	53.6 \pm 3.8
Kattegat (Klint)	2	0.5	100	102.8 \pm 7.2
Norwegian Sea (A)	10	0.5	0	4.2 \pm 0.3
Norwegian Sea (A)	300	0.5	0	4.4 \pm 0.3
Norwegian Sea (A)	500	0.5	0	4.7 \pm 0.3
Norwegian Sea (A)	1000	0.5	0	4.3 \pm 0.3
Norwegian Sea (B)	5	0.5	0	4.3 \pm 0.3
Norwegian Sea (C)	5	0.5	0	4.5 \pm 0.3
Norwegian Sea (D)	8	0.5	0	4.4 \pm 0.3

* The results are shown as the measured values \pm 7% uncertainty of whole analysis procedure.

3.4. Chemical speciation of technetium in natural seaweed

As common aquatic plants, seaweeds, especially brown seaweeds like *Fucus* genus, have been proven to be very effective to uptake technetium from seawater and thus widely used as bio-indicators for monitoring of ^{99}Tc in the marine environment [10,78,82,84]. Although there are some studies on the enrichment of technetium by seaweed [9,84], the mechanism of technetium uptake and

accumulation in seaweed is still not clear. The information on chemical speciation of technetium in seaweed are helpful to understand the storage and accumulation, as well as uptake of technetium in natural seaweed.

In this work, an analytical method for chemical speciation of ^{99}Tc in natural seaweed has been developed. Different species of technetium were separated using biochemical techniques and detected by ICP-MS after sample pre-treatment and purification of technetium using extraction chromatographic technology. The possible uptake mechanisms of technetium in seaweed were deduced. To our best knowledge, this is the first report for comprehensive investigation of technetium speciation in natural seaweed.

3.4.1. Separation of various technetium species and their measurement

Chemical species of technetium in brown seaweed

According to the tracer studies by Garten and co-workers [67], technetium can be occur in pigments, polysaccharides, hemicelluloses and cellulose of maple leaves. Besides inorganic anion TcO_4^- , technetium was also observed in proteins, cysteine as well as glutathione of tomato and spinach plants [65,66]. As a common aquatic plant, brown seaweed has the normal cell structure of plant. Besides the water and inorganic salts, most components of seaweed are organic compounds, which mainly include low molecular carbohydrates like mannitol and macromolecules such as protein, algin, cellulose and others. A reported distribution of different chemical components in brown seaweed (*Fucus evanescens*) is shown in Figure 16. Accordingly, the reduced technetium in cells of brown seaweed might be combined with these organic compounds and form complexes such as Tc-protein, Tc-algin, Tc-cellulose, and Tc-pigment. Of course, some TcO_4^- might be also contained in brown seaweed. The purpose of present work is to identify and quantify these technetium species.

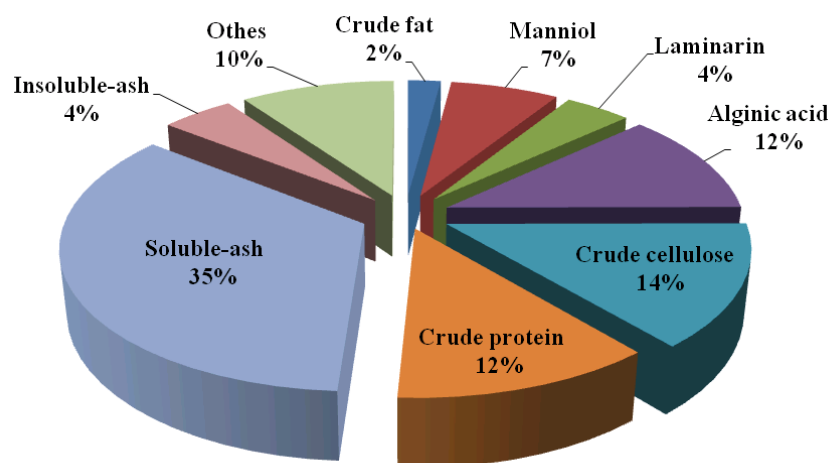


Figure 16. Distribution of different chemical components in brown seaweed *Fucus evanescens* (dry mass). The data was adopted from [85].

Separation and measurement of various chemical species of technetium

Based on their chemical properties, different species of technetium can be leached with chemical reagents such as organic solvent, buffer solution, and acid and alkali solutions using the procedures presented in Figure 6. The leaching conditions (including leaching time, temperature and the ratio for mass of fresh seaweed to volume of leaching solution) were modified according to the report by Hou et al. [86] and applied for the extraction experiment in this work.

In brown seaweed, pigments such as chlorophyll are normally soluble in some organic solvents such as acetone, ether and methanol, but insoluble in water. In the present work, pigments were first leached from fresh brown seaweed (*Fucus vesiculosus*) with acetone at room temperature. It was observed that after 3 times leaching with acetone, the remained residue becomes almost colorless, indicating that almost all of pigments have been extracted from *Fucus vesiculosus*. Because fresh sample was used, besides acetone, water in the fresh seaweed is also separated from residue and mixed with acetone phase, TcO_4^- and some other water-soluble technetium species (low oxidation state of technetium species) in the seaweed water might enter into the acetone leachate. This fraction of technetium has to be removed to avoid an overestimation of pigments associate technetium, and unreliable analytical results. To remove water-soluble technetium species, NaCl powder is added to the acetone leachate to obtain saturated NaCl aqueous solution which is immiscible with acetone and forming two-phase of saturated NaCl solution and acetone. After removal of acetone by evaporation, the main compound of residue is pigment. It should be mentioned that besides pigments, other fatty materials such as vegetable fat and free fatty acid can also be extracted by acetone, however, the amount of these kinds of compounds is very limited [86].

According to the report by Whyte et al. [87], besides inorganic compounds, almost all mannitol, most of fucoidan, some of protein, hydrophobic and polymeric material in *Macrocystis integrifolia* (brown seaweed) are water-soluble. For brown seaweed *Fucus vesiculosus*, similar components might be present. Considering the special chemical property of protein, tris-HCl buffer solution ($\text{pH} \approx 7.5$) was applied to leach water-soluble technetium species. To reduce the viscosity of leachate during separation of protein, some amount of CaCl_2 was added in buffer solution ($\sim 1\%$ wt.) to fix algin (the main compound in brown seaweed) by formation of insoluble calcium alginate. There are more than thousand kinds of proteins in seaweed [85]. The water solubility and amino-acid sequence of these proteins are different, which can be used to separate various proteins [86]. To investigate the combination of technetium with protein, water-soluble proteins were separated by salting out protein precipitate with $(\text{NH}_4)_2\text{SO}_4$, which was often used for protein extraction in biochemistry [85]. The $(\text{NH}_4)_2\text{SO}_4$ powder was added slowly during continuous stirring till a 95% saturation of $(\text{NH}_4)_2\text{SO}_4$ was reached, and then the solution was stirred for 30 min and allowed to stand for 24 h at room temperature to get protein precipitate. After removing the protein fraction by centrifuge, the supernatant was directly loaded into a conditioned anion exchange column (7 mL AG1- \times 4 resin, particle size 50-100 μm) to separate TcO_4^- from other water-soluble technetium species. $^{99\text{m}}\text{TcO}_4^-$ was added to monitor the yield of TcO_4^- during column separation. It was found that almost all of TcO_4^-

(>95%) can be adsorbed onto the resin although high concentration of SO_4^{2-} contained. Considering the high sorption ability of TcO_4^- , the column was washed with relatively high concentration of HNO_3 (e.g., 1 mol/L) to remove other technetium species which are easily desorbed from the resin. Elution behaviour of TcO_4^- on AG1- \times 4 column was investigated. The results (Figure 17) show that 70 mL of 8 mol/L of HNO_3 is enough to elute all of TcO_4^- from column. Although there is no direct evidence that all of absorbed technetium species on the column is just TcO_4^- , the good agreement between total water-soluble technetium and the sum of different fractions of technetium after the column separation (see Table 5) indicates that the species of technetium in the eluate from the column should be TcO_4^- , at least with a similar behaviour as TcO_4^- . Technetium in effluent and washes from the column are mainly other water-soluble technetium.

Table 5. Chromatographic separation of different water-soluble technetium species *

Concentration of water-soluble technetium species (mBq/g dry weight (total mass of seaweed))				
Samples	Species of water-soluble technetium			Total technetium in water-soluble fraction (direct measurement)
	TcO ₄ ⁻ (eluate)	Other water-soluble species (effluent and washes)	Sum	
1 #	5.3±0.5	6.7±0.7	12.0±0.9	12.0±1.2
2 #	5.1±0.5	6.8±0.7	11.9±0.9	12.1±1.2

* Same sample solutions were used during column separation and direct measurement. The results are presented as the measured values \pm 10% uncertainties estimated in the whole analytical procedure.

By leaching the residue (after buffer solution extraction) with 50 mL of 0.2 mol/L HCl at 60 °C (3 times), acid-soluble technetium can be obtained. According to Ji [85], the acid-soluble fraction of seaweed mainly includes water-insoluble laminaran and fucoidan, and acid-soluble proteins. Because alginic acid is not soluble, there is no algin extracted in acid leaching. The reduced technetium species might combine with these compounds. In the present work, different species of technetium in this fraction were not further separated, and only total acid-soluble technetium was investigated.

Algin is the major component of brown seaweed. It mainly exists as alginic acid, and its calcium, magnesium, potassium and strontium salts. Alginic acid and its di- and tri-valent metal salts (except magnesium and mercury) are insoluble in water, whereas, its potassium, sodium and magnesium salts are water-soluble [85]. Thus algin is usually extracted by a Na_2CO_3 (or K_2CO_3) solution via converting insoluble alginate into its soluble sodium or potassium salts. In this work, algin remains in the residue by formation of insoluble calcium alginate and alginic acid during leaching with buffer solution and HCl solution, respectively. 0.3 mol/L Na_2CO_3 solution was used to extract algin at 60 °C; in this case, almost all of algin can be extracted in the form of soluble sodium alginate [86], which means that all of Tc-algin species can be obtained if these kinds of Tc-complexes formed. It should be pointed out that Na_2CO_3 solution is an alkali media (pH \approx 10), besides Tc-algin, some other technetium species (soluble in alkali media, such as alkali-soluble protein) can also be extracted. After precipitation of algin by formation of alginic acid, the supernatant was kept and combined with NaOH extraction solution to get alkali-soluble technetium species. Because the cell wall can be efficiently destroyed in alkali solution, most of hemicellulose and some alkali-soluble protein will be extracted

into this solution [67]. There is still some residue after extraction with NaOH solution at relatively high temperature (e.g., 60 °C). According to the report by Ji [85], this kind of substance is mainly cellulose, which is the main component of the cell wall. The remained technetium in this fraction should be cellulose associated technetium species.

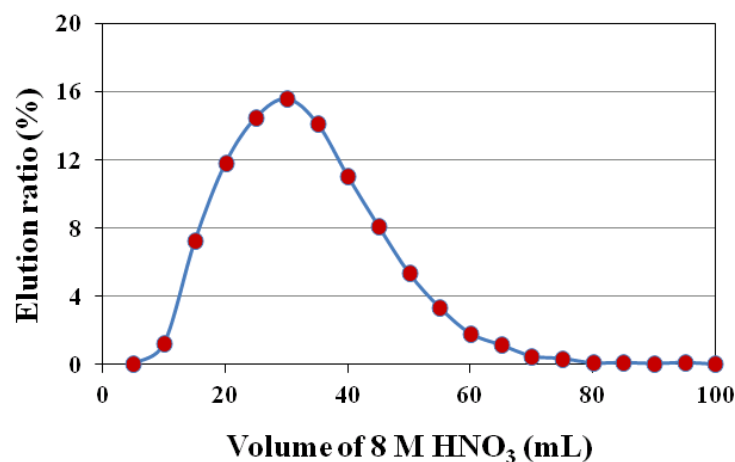


Figure 17. Elution curve of TcO_4^- from AG1- \times 4 anion exchange column (7 mL resin) using 8 mol/L HNO_3 with flow rate of 2 mL/min.

After separation of the different species/fractions of technetium in *Fucus vesiculosus*, a series of sample pre-treatment methods were applied (see details in **Experimental section**). ^{99}Tc in each samples was measured by ICP-MS after extraction chromatographic separation and purification. The analytical results for different species of technetium in a natural brown seaweed are shown in Table 6.

Table 6. Distribution of technetium in various species/fractions in *Fucus vesiculosus* *

Species/fraction of technetium	Concentration of technetium (mBq/g dry weight (total mass))	Percentage of each technetium species/fraction in whole sample (%)
Tc-pigment	0.5 \pm 0.1	2.8 \pm 0.4
TcO_4^-	2.7 \pm 0.4	14.6 \pm 2.2
water-soluble Tc-protein	ND	–
other water-soluble Tc	5.5 \pm 0.8	29.1 \pm 4.4
acid-soluble Tc	2.6 \pm 0.4	13.9 \pm 2.1
Tc-algin	2.0 \pm 0.3	10.7 \pm 1.6
other alkali-soluble Tc	4.8 \pm 0.7	25.4 \pm 3.8
Tc-cellulose	0.6 \pm 0.1	3.2 \pm 0.5
Sum	18.7 \pm 2.8	99.6 \pm 14.9
Total	18.7 \pm 0.9	

* Technetium was not detected in water-soluble protein. Except total concentration of technetium (2SD of uncertainty), all other results are presented as the measured values \pm 15% uncertainties estimated in the whole analytical procedure.

3.4.2. The behaviour of various technetium species in seaweed

Based on the developed separation methods, different species of technetium have been investigated. Unlike iodine (large amount of iodine is combined with proteins) [88], technetium in *Fucus vesiculosus* shows a relatively uniform distribution and various species of technetium including TcO_4^- , Tc-pigment, Tc-algin and Tc-cellulose and different fractions such as water-soluble, acid-soluble and alkali-soluble technetium have been observed. These technetium species, to a certain extent, might control the behaviour of technetium in seaweed.

Inorganic anion of TcO_4^-

TcO_4^- is a very important inorganic anion of technetium, and dominated technetium species in seawater. It has been reported that TcO_4^- is the only technetium species known to be taken up by plants [56,89]. In the present work, some amount of TcO_4^- (about 15% of total ^{99}Tc) was found in fresh *Fucus vesiculosus*. The results are similar as the reported values of TcO_4^- (about 20%) in the leaves of tomato plants [65]. The water content accounts up to more than 70% (mass ratio) in fresh *Fucus vesiculosus*. Once uptake from seawater, TcO_4^- might be transferred through cells wall and dispersed in the water phase in seaweed and then reduced and fixed. It has been reported that the concentration of TcO_4^- in the cell of duckweed determines the reduction of technetium [56]. To this point, the presence of some amount of TcO_4^- in seaweed is necessary and might be treated as a link between technetium in culture solution (e.g., seawater) and that fixed in seaweed. By investigation on the behaviour of TcO_4^- in the roots of tomato plants, Krijger and co-workers reported that TcO_4^- concentration in the roots is approximately five times higher than the initial concentration in the nutrient solution and an active uptake process for TcO_4^- was proposed [65]. For *Fucus vesiculosus*, if 70% water (mass ratio), 15% of TcO_4^- content (activity ratio of total ^{99}Tc) and a concentration factor of 1×10^5 L/kg dry weight were considered, the ratio of concentrations of TcO_4^- in seaweed and seawater can be reached up to 2×10^4 , indicating a strong active uptake process.

Pigment associated technetium

Pigments are a kind of lipid compounds in seaweed. They can be extracted from fresh seaweed by organic solvents such as acetone. The results show that about 3% of total technetium in *Fucus vesiculosus* was contained in the pigment fraction, indicating that technetium can be associated with pigment although the total amount is rather low. Similar results have been reported by Garten and co-workers when investigating species of technetium in leaves of maple trees [67]. Although there are many unsaturated conjugated double bonds and replaceable sites existing in lipid compounds, it seems that technetium is difficult to combine with these sites [2]. However, electron donors such as $-\text{N}$ or $-\text{S}$ in the pigment molecules might combine some reduced technetium species through formation of Tc-N or Tc-S bonds [2].

Complex of technetium with nitrogenous compounds

Protein is a very important nitrogenous compound in plants. There are more than thousand different proteins existing in seaweed, of which some are water-soluble, and others are acid or even alkali-soluble based on their different spatial structures and properties [85,90]. Hou and co-workers investigated the water-soluble species of iodine in algae and reported that most organic iodine is associated with protein [88]. Because of the special functional groups (amino-acid) contained in protein, low oxidation state of technetium might be combined with these groups through formation of Tc-N or Tc-O bonds [2]. An investigation of Tc-protein species in the water-soluble fraction was carried out in this work. It is interesting that technetium shows different behaviour compared to iodine and cannot be found in protein in the species of seaweed investigated. This may be explained by that the obtained water-soluble proteins are low molecular types, which might be not easy to combine with technetium or the formed technetium complex with low molecular protein is not stable, and a ligand exchange to macromolecules such as glutathione and cysteine might be followed [65].

Besides proteins, some other nitrogenous compounds such as polypeptides are also presented in natural seaweed [85]. These kinds of compounds usually have the similar functional groups as protein, and thus might combine with the reduced technetium. According to the report by Krijger et al. [65], reduced technetium complexes first to non-thiol groups of proteins at the place of reduction, and is subsequently stabilized by the -SH groups of glutathione and cysteine. Harms et al. investigated species of technetium in spinach plants and reported that the reduced technetium has a high affinity for cysteine groups, and about 25% of total technetium is containing in cysteine of spinach leaves [66]. This might explain the observed association of technetium with cysteine and glutathione of tomato plants [65]. However, because there is no relevant work on Tc-polypeptide species in natural seaweed, the potential combination of technetium with these kinds of nitrogenous compounds in seaweed are still not clear and need to be further studied.

Complex of technetium with carbohydrate

Carbohydrate is the main component of marine algae, it accounts to 30-50% of total dry mass of seaweed [85]. In brown seaweed such as *Fucus genus*, algin, laminarin, fucoidan, cellulose and mannitol are the common carbohydrate compounds.

Mannitol is a low molecular carbohydrate in seaweed, it is easily dissolved in water, and has a relatively high level in *Fucus genus* (about 7% in *Fucus evanescens*) (Figure 16). Because of the active hydroxyl hydrogen and weak steric (small molecular), the reduced technetium might replace the hydroxyl hydrogen and form complexes with several mannitol molecules through formation of Tc-O bonds [2]. However, because mannitol was not separated in this work, it is difficult to confirm that the water-soluble TcX is mainly Tc-mannitol. To clarify technetium behaviour in seaweed, further investigation on the water-soluble of technetium species is necessary.

As a major component of cell wall, algin widely exists in brown seaweed, and more than 15% of algin (mass ratio of dry mass) was found in *Fucus vesiculosus* in this work. Unlike iodine (iodine does not bind with algin) [88], some amount of technetium (more than 10% of total ^{99}Tc in *Fucus*

vesiculosus) was observed in algin, indicating that reduced technetium might be combined with algin through formation of complexes. Algin is one kind of polysaccharide polymer, and dextran is its basic structure unit, in which carbonyls are combined but carboxyls are free. Although there is no branched chain and unsaturated C-C bond in algin, because of the existing of active carboxyl as well as hydroxyl oxygen, complexes will be formed between high valance of metal cations and different algin molecules [85]. Accordingly, complexes of technetium with algin might be formed when the reduced technetium is in cationic form (e.g., Tc^{4+}). Compared with algin, the amount of technetium contained in cellulose is low (about 3%) (Table 6), although relatively high amount of cellulose is presented in seaweed (about 12%, mass ratio of dry *Fucus vesiculosus*), indicating that the formation of complexes between cellulose and reduced technetium is limited. Algin and cellulose have a similar structure unit but different functional groups, i.e. carboxyl for algin and hydroxyl for cellulose (Figure 18). The different amount of technetium observed in algin and cellulose indicates that the carboxyl, especially carboxyl oxygen might be the main bonding site with technetium through formation of Tc-O bond in these kinds of compounds. Besides algin and cellulose, fucoidan and laminarin are also present in brown seaweed although the amounts of these two kinds of carbohydrates are low [85]. Among these, fucoidan mainly exists in the matrix of cell wall while laminarin presents in the cytoplasm. Because the fucoidan and laminarin fractions were not separated in the present work, the combination of technetium with these kinds of carbohydrates are still not clear and need to be further investigated.

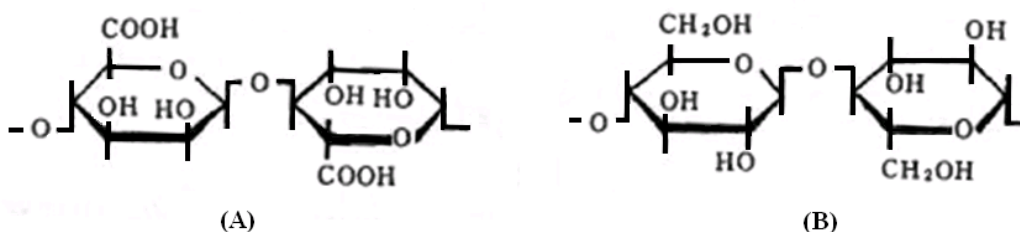


Figure 18. Structure units of (A) alginic acid and (B) cellulose (adopted from [85])

4. Conclusions and perspective

^{99}Tc is one of the most important fission products released into the biosphere by human nuclear activities. Study on the analysis of ^{99}Tc and its speciation is therefore a key issue for its behaviour in ecosystem. In this thesis, series of analytical methods have been established for rapid and accurate determination of total ^{99}Tc in environmental samples, as well as speciation analysis of technetium in seaweed. The application of ^{99}Tc as an oceanographic tracer to monitor seawater movement and coastal pollution using seaweed as a bio-indicator was also investigated. The main conclusions are presented as following.

(i) No significant loss of technetium was observed during ashing of seaweed (≥ 1 g dry weight, without any pre-treatment) under $800\text{ }^{\circ}\text{C}$ for less than 6 h. Pre-treatment of seaweed samples (< 1 g dry weight) with addition of some KCl or NaCl and diluted NaOH solution is required before ashing. The optimal conditions for seaweed ashing are at $700\text{ }^{\circ}\text{C}$ for 3h. Soil and sediment samples can be ashed at $550\text{ }^{\circ}\text{C}$ for 3 h without any pre-treatment. Technetium was proved to be more stable in alkali media during evaporation. In HNO_3 media, technetium solution should be evaporated at lower temperature (e.g., $< 100\text{ }^{\circ}\text{C}$) if the solution needs to be evaporated to dryness or keep some solution left (e.g., 0.5 mL) at relatively high temperature (e.g., $> 100\text{ }^{\circ}\text{C}$). For HCl media, especially with high concentration of HCl, the sample solution should not be completely evaporated to dryness even at lower temperature (e.g., $< 100\text{ }^{\circ}\text{C}$).

(ii) The distribution coefficient of TcO_4^- onto TEVA resin in HNO_3 media decreased with the increase of HNO_3 concentration. A procedure of loading sample solution (contained TcO_4^-) onto TEVA column in low concentration HNO_3 media (e.g., $< 0.1\text{ mol/L}$) and elution of TcO_4^- at high concentration of HNO_3 (e.g., $> 8\text{ mol/L}$) was thus applied. The concentration of H^+ is the main factor affecting the sorption of TcO_4^- onto TEVA resin. The elution of TcO_4^- from TEVA column with a high concentration of HNO_3 might be attributed to the formation of HTcO_4 at high concentration of H^+ and the replacement of TcO_4^- by NO_3^- , in which the formation of HTcO_4 is dominant factor.

(iii) Pre-treatment of loading solution with 30% H_2O_2 in alkali media can significantly improve the removal of ruthenium during chromatographic separation using a TEVA column. This might be attributed to the reduction of ruthenium in this process. With the application of two small TEVA columns (1.5 mL for each), a sufficient removal of isobaric interferences with decontamination factors of $> 10^4$ for molybdenum and $> 10^5$ for ruthenium, and whole recovery of 60-95% for technetium were achieved for different environmental samples. An absolute detection limit of 1.5 mBq for ^{99}Tc was obtained by ICP-MS measurement. With the sequential injection approach employing TEVA columns and ICP-MS measurement, the duration of developed procedures was remarkably reduced, and a batch of samples ($n > 4$) can be analyzed with 24 h. The developed analytical methods were proven to be reliable and can be used to determine low-level ^{99}Tc in environmental samples.

(iv) Different species of technetium in *Fucus vesiculosus* were separated using biochemical techniques and detected by ICP-MS after sample pre-treatment and purification of technetium using

TEVA columns. Technetium speciation in *Fucus vesiculosus* show a relatively uniform distribution. Besides the inorganic anion TcO_4^- and some other water-soluble technetium species, more than half of total technetium in *Fucus vesiculosus* was found to be water-insoluble, and can be extraced by acid and alkali solutions. In addition, some amount of technetium was also found in pigment and cellulose fractions. The formation of complexes between reduced technetium and biological macromolecules of seaweed might be the reason for technetium uptake.

(v) Seasonal variation of ^{99}Tc concentration in *Fucus vesiculosus* was observed with a higher concentration in winter and lower concentration in summer. Dilution of ^{99}Tc concentration in seawater by less contaminated water mass due to water exchange and movement as well as runoff of the fresh water from land might be the main reason driving the seasonal cycle of ^{99}Tc concentration in seaweed. Concentration factors of ^{99}Tc in seaweed show a relatively constant value and are independed on sampling date. A mean value of $(1.9 \pm 0.5) \times 10^5$ L/kg dry weight for *Fucus vesiculosus* to technetium was obtained, which is about one order of magnitude higher than that for rhenium $((2.1 \pm 0.3) \times 10^4$ L/kg dry weight). The above information is important for application of *Fucus vesiculosus* as a bio-indictor to monitor the pollution of seawater and estimate the temporal variation and dispersion of pollution in the marine system.

The investigation on the behaviour of ^{99}Tc in the ecosystem will still be an attractive topic in the future. Although a number of analytical methods have been developed for total technetium analysis, the procedures, to a certain extent, are still operated manually, especially during sample pre-treatment stages which usually take much time of the whole analytical procedure. Therefore fully automated analysis methods will be the major future challenge for analysis of ^{99}Tc in environmental samples. Because of the limitation of detection limit of ICP-MS and β counting such as LSC and gas flow GM counter, large volume of environmental samples are usually needed, which is relatively laborious for sampling as well as analysis work in the laboratory. With the increased numbers of AMS facilities installed in the recent years, the application of this technique for ^{99}Tc measurement will become more popular and much lower level of ^{99}Tc can be detected with small sample size. Speciation analysis is a field of research which is still rather fresh and thus possesses the attractive power in future research. Because of the low levels of ^{99}Tc , the investigation on technetium speciation in environmental samples using traditional technique (e.g., EXAFS) is not possible. Chemical separation and ICP-MS or AMS measurement might be a more effective way in this case. Although some methods can be used for separation of different technetium speciation, the purification and certification of separated technetium species are still an issue and a lot of work need to be done in future.

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Determination of technetium-99 in environmental samples: A review

Analytica Chimica Acta 2012, 709, 1-20



Review

Determination of technetium-99 in environmental samples: A review

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ARTICLE INFO

Article history:

Received 30 June 2011

Received in revised form 11 October 2011

Accepted 11 October 2011

Available online 18 October 2011

Keywords:

Technetium-99

Radionuclide

Analytical procedure

Environmental samples

Automated analysis

Review

ABSTRACT

Due to the lack of a stable technetium isotope, and the high mobility and long half-life, ⁹⁹Tc is considered to be one of the most important radionuclides in safety assessment of environmental radioactivity as well as nuclear waste management. ⁹⁹Tc is also an important tracer for oceanographic research due to the high technetium solubility in seawater as TcO_4^- . A number of analytical methods, using chemical separation combined with radiometric and mass spectrometric measurement techniques, have been developed over the past decades for determination of ⁹⁹Tc in different environmental samples. This article summarizes and compares recently reported chemical separation procedures and measurement methods for determination of ⁹⁹Tc. Due to the extremely low concentration of ⁹⁹Tc in environmental samples, the sample preparation, pre-concentration, chemical separation and purification for removal of the interferences for detection of ⁹⁹Tc are the most important issues governing the accurate determination of ⁹⁹Tc. These aspects are discussed in detail in this article. Meanwhile, the different measurement techniques for ⁹⁹Tc are also compared with respect to advantages and drawbacks. Novel automated analytical methods for rapid determination of ⁹⁹Tc using solid extraction or ion exchange chromatography for separation of ⁹⁹Tc, employing flow injection or sequential injection approaches are also discussed.

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Abbreviations: AMS, accelerator mass spectrometry; DIHEN, direct injection high efficiency nebulizer; EARP, enhanced actinide removal plant; EDTA, ethylenediaminetetraacetic acid; GBq, giga becquerel, 10^9 Bq; GM, Geiger-Müller; HR, high resolution; ICP-MS, inductively coupled plasma mass spectrometry; ICP-QMS, inductively coupled plasma quadrupole mass spectrometry; ICP-SFMS, inductively coupled plasma sector field mass spectrometry; K_{sp} , solubility product; LSC, liquid scintillation counting; MCN, microconcentric nebulizer; MS, mass spectrometry; NAA, neutron activation analysis; PBq, peta becquerel, 10^{15} Bq; RIMS, resonance ionization mass spectrometry; TBP, tri-butylphosphate; TBq, tera Becquerel, 10^{12} Bq; ETV, electrothermal vaporization; TEVA, TEVA-SpecTM resin; TiOA, tri-isooctylamine; TIMS, thermal ionization mass spectrometry; TOA, trioctylamine; USN, ultrasonic nebulizer.

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1. Introduction

Technetium (Tc), atomic number of 43, has no stable isotope and is generally considered as an “extinct” element on the earth. Tc was first synthesized and isolated by Perrier et al. in 1937 as a product from the bombardment of molybdenum with deuterons or neutrons [1]. So far 45 isotopes of Tc, ranging from ^{85}Tc to ^{117}Tc , have been synthesized, and most of them are short-lived isotopes with half lives of less than 1 h. Table 1 lists the isotopes of Tc with half lives exceeding one hour. Of these, ^{97}Tc ($t_{1/2} = 2.6 \times 10^6 \text{ y}$), ^{98}Tc ($t_{1/2} = 4.2 \times 10^6 \text{ y}$) and ^{99}Tc ($t_{1/2} = 2.1 \times 10^5 \text{ y}$) are the most long-lived. Both ^{97}Tc and ^{98}Tc are mainly formed by activation reactions of neutrons or charged particles, although very small amounts have been produced in anthropogenic nuclear processes, and negligible amounts of ^{97}Tc and ^{98}Tc occur in the environment. ^{99}Tc can be produced by thermal neutron induced fission of ^{235}U with a relatively high accumulated fission yield of 6.06%, making ^{99}Tc relatively high abundant among fission products [2,3]. A large amount of ^{99}Tc has been produced and released to the environment from nuclear installations, which makes ^{99}Tc the only environmentally significant Tc isotope. Meanwhile ^{99}Tc can also be produced through neutron activation of ^{99}Mo . Fig. 1 shows the formation scheme of ^{99}Tc .

The interest in investigating ^{99}Tc in environmental samples results partly from the absence of a stable Tc isotope. ^{99}Tc as the completely dominating isotope of Tc is thus the only isotope available for studying the unknown environmental and biological behaviour of this element. Due to its high mobility, high fission yield, and long half-life, ^{99}Tc is one of the most important

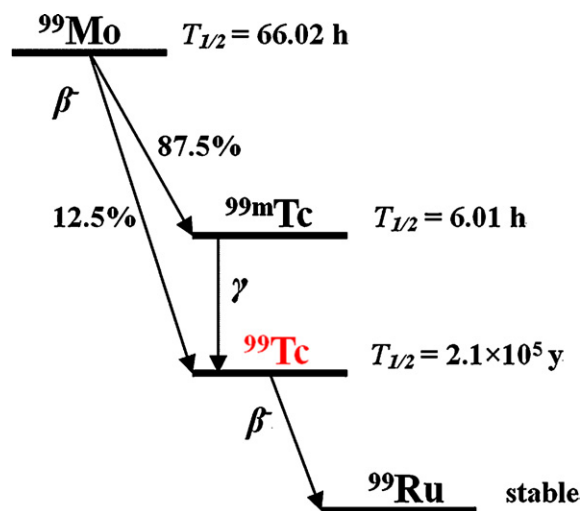


Fig. 1. Decay scheme of ^{99}Mo .

radionuclides in safety assessment of radioactivity in the environment, as well as in decommissioning of nuclear facilities and management of nuclear waste. The high water solubility of Tc (in the form of TcO_4^-) and the long half life of ^{99}Tc , and thus long residence time in the oceans, make ^{99}Tc an ideal oceanographic tracer for investigation of movement, exchange and circulation of water masses. All these investigations and applications require an accurate determination of ^{99}Tc in various types of samples.

^{99}Tc is a pure β^- emitter with the maximum decay energy of 0.294 MeV. It can therefore be measured by radiation counting [4–9]. The β counting using gas flow Geiger–Müller (GM) counter and liquid scintillation counter (LSC) are the main techniques for ^{99}Tc measurement. Due to the interference of matrix components and the spectrometric interference from other radionuclides, especially β emitters, a thorough chemical separation of ^{99}Tc from the matrix and other radionuclides is required before measurement. Anion exchange chromatography and co-precipitation are widely used to pre-concentrate ^{99}Tc from samples [5,6]. For further purification, solvent extraction is often utilized to separate ^{99}Tc from other interfering radionuclides. In recent years, extraction chromatography using TEVA-Spec™ (TEVA) resin has been employed to purify ^{99}Tc from the interfering radionuclides [10–13]. The long half-life, and therefore low specific activity, of ^{99}Tc (0.64 Bq ng^{-1}) makes mass spectrometry (MS) a potentially sensitive method for measurement of ^{99}Tc . Accelerator mass spectrometry (AMS) [14–16], thermal ionization mass spectrometry (TIMS) [17] and inductively coupled plasma mass spectrometry (ICP-MS) [18–21] have been applied for ^{99}Tc measurement. Among these MS techniques, ICP-MS is the most widely and frequently used mass spectrometric method for measurement of ^{99}Tc in many types of environmental samples due to its low cost and easy accessibility. The main challenge in ^{99}Tc measurement by ICP-MS is the interferences of isobars and molecular ions. At mass 99, isobaric interferences from the stable isotope ^{99}Ru and the molecular ion $^{98}\text{Mo}^1\text{H}$ are the main interferences in the measurement of ^{99}Tc using ICP-MS. Highly efficient methods for purification of ^{99}Tc from these interferences before measurement are necessary. The chemical separation techniques used for radiometric methods can also be applied in the mass spectrometric determination of ^{99}Tc . The main difference is that the separation methods used for mass spectrometric measurement focuses on the removal of stable isotopic interferences with the mass of 99 AMU [22]. This article aims to discuss and critically compare various analytical methods for the determination of ^{99}Tc in the environment. New developments of

Table 1

Nuclear properties of technetium isotopes with a half-life more than 1 h.

Isotopes	Half-life	Decay mode	β E _{max} (keV)	Main γ -X-ray energy (keV) (intensity)
⁹³ Tc	2.8 h	EC + β^+	–	γ (1363.0, 66%; 1520.4, 24.4%)
⁹⁴ Tc	4.9 h	EC + β^+	–	γ (702.6, 99.6%; 849.7, 95.7%; 871.1, 100%)
⁹⁵ Tc	20.0 h	EC + β^+	–	γ (765.8, 93.8%); X-ray (17.5, 56.5%)
^{95m} Tc	61.0 d	EC + β^+ , IT	–	γ (204.1, 63.3%; 582.1, 30%; 835.1, 26.6%)
⁹⁶ Tc	4.3 d	EC + β^+	–	γ (778.2, 100%; 812.6, 82%; 849.9, 98%)
⁹⁷ Tc	2.6×10^6 y	EC	–	–
^{97m} Tc	90.1 d	EC, IT	–	X-ray (18.4, 27%)
⁹⁸ Tc	4.2×10^6 y	β^-	398.2 (100%, β^-)	γ (652.4, 100%; 745.4, 102%)
⁹⁹ Tc	2.1×10^5 y	β^-	293.7 (100%, β^-)	–
^{99m} Tc	6.0 h	β^- , IT	–	γ (140.5, 89%)

automated and rapid analytical methods for determination of ⁹⁹Tc are also discussed.

1.1. Source term of technetium-99 in the environment

In nature ⁹⁹Tc can be produced by spontaneous fission of ²³⁸U and neutron induced fission of ²³⁵U in the earth [23,24]. ⁹⁹Tc can also be produced by cosmic ray reactions with Mo, Ru and Nb in the earth crust. It has been estimated that these two types of processes have produced about 60 PBq (6×10^{16} Bq) of ⁹⁹Tc. This ⁹⁹Tc is mainly distributed in the crust, and not in the surface environment. In addition, due to the relatively long half-life of ⁹⁹Tc, the concentration of the naturally produced ⁹⁹Tc in the surface environment is too low to be detected. At present, almost all ⁹⁹Tc in the environment results from anthropogenic nuclear activities, mainly from nuclear weapons testing, reprocessing of spent nuclear fuel, nuclear accidents, nuclear power plants and medical application of ^{99m}Tc [25,26]. It has been estimated that the atmospheric nuclear weapons testing in 1940s–1970s has released about 140 TBq (1.4×10^{14} Bq) of ⁹⁹Tc to the environment [27], which is mainly deposited in the northern hemisphere. Compared with the atmospheric nuclear tests, a large number of nuclear tests were carried out underground, which produced a relatively larger amount of ⁹⁹Tc, but most of this was kept underground. It was estimated that about 21 TBq of ⁹⁹Tc was released in the underground nuclear tests in Nevada, USA, and 2.5 TBq of ⁹⁹Tc in French Polynesia [28]. Up to now, a huge amount of ⁹⁹Tc has been produced during the operation of the nuclear power plants. It has been estimated that 16–19 PBq ($(1.6\text{--}1.9) \times 10^{16}$ Bq) of ⁹⁹Tc had been produced worldwide up to the mid 1980s [29]. It was calculated that the production rate of ⁹⁹Tc in nuclear power plants is about 5.8 TBq (GW(th)y)^{−1} [30]. About 7.2 TW(e)y electric power has been produced in nuclear power plants from 1971 to 2006 [31], which has resulted in a production of about 140 PBq of ⁹⁹Tc, assuming about 30% conversion efficiency of thermal energy to electricity. However, most of this ⁹⁹Tc was captured in the elements of the nuclear fuel, and not released to the environment. It was estimated that only 4 GBq (4×10^9 Bq) ⁹⁹Tc was released from the nuclear power plants until 1990. This was mainly due to the small leakage of the nuclear fuel and relatively small amount of uranium impurities in cooling water and construction materials in the nuclear power reactors. It can therefore be estimated that less than 10 GBq of ⁹⁹Tc was released from the nuclear power up to 2010 considering the gradually increasing number of nuclear power plants over the past 20 years. However, the release of ⁹⁹Tc from the spent fuel reprocessing is the main source of ⁹⁹Tc in the environment. Many spent nuclear fuel reprocessing plants have been operated or are in operation. Among these the most important ones are those at Sellafield (UK), La Hague (France), Marcoule (France), Mayak (Russia), Kalpakkam (India), Rokkasho (Japan), Hanford (USA) and Savannah (USA). Up to 2009, the Sellafield reprocessing plant has discharged 1720 TBq of ⁹⁹Tc to the Irish Sea, and the La Hague reprocessing plant has

discharged about 154 TBq of ⁹⁹Tc to the English Channel. Fig. 2 shows the annual discharges of ⁹⁹Tc from two European reprocessing plants (Sellafield and La Hague) [32]. No data on ⁹⁹Tc discharge from other reprocessing plants is available. ^{99m}Tc has been widely applied for medical diagnosis and medical research since its first application in the hospital in 1960. It is exclusively supplied by ⁹⁹Mo–^{99m}Tc generators. It is estimated that about 22 PBq y^{−1} of ⁹⁹Mo is required in 2010 for producing the generators to meet the world-wide requirement of medical ^{99m}Tc. The ⁹⁹Mo will decay to ^{99m}Tc and finally to ⁹⁹Tc, releasing 0.78 GBq y^{−1} of ⁹⁹Tc to the environment by excretion from the patients at 2010 level. However, a smaller amount of ⁹⁹Tc was released in the early years, which was estimated to be only about 0.20 GBq y^{−1} [33]. The total ⁹⁹Tc released from this type of sources can be estimated to be less than 20 GBq, assuming a maximum release of 0.78 GBq y^{−1} in 1990–2010 and 0.20 GBq y^{−1} in 1970–1990. ⁹⁹Tc can also be released to the environment in nuclear accidents. It was estimated that the Chernobyl accident in 1986 has released about 0.75 TBq of ⁹⁹Tc to the environment [34]. Although the contribution of this source on a global scale is less important than other sources, the effect on the ⁹⁹Tc level in local area might be still significant. The Fukushima nuclear accident that took place in March 2011 might also have released some amount of ⁹⁹Tc to the environment. The estimated atmospheric releases of 30 PBq of ¹³⁷Cs corresponds to about 1/3 of the estimated ¹³⁷Cs releases from Chernobyl accident. It might be estimated that the releases of ⁹⁹Tc to the atmosphere from the Fukushima accident is about 0.25 TBq. However, besides the atmospheric releases, a large volume of waste water was discharged to the sea during the accident; but no data on ⁹⁹Tc discharge to the sea by this way is available at present. It can be concluded that the major source of ⁹⁹Tc in the environment is the nuclear reprocessing plants, which accounts for more than 90% of the ⁹⁹Tc in the environment. Table 2 summarizes the major sources of ⁹⁹Tc in the environment.

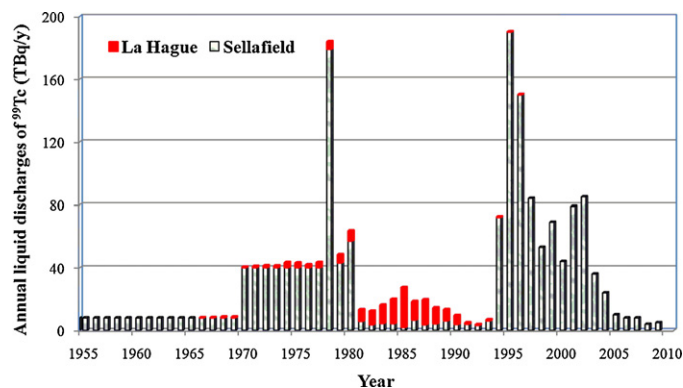


Fig. 2. Liquid discharges of ⁹⁹Tc from two European reprocessing plants at Sellafield (UK) and Cap de La Hague (France) to the marine system [32].

Table 2
Main sources of ^{99}Tc in the environment.

Source	^{99}Tc released ($\times 10^{12}$ Bq)	Reference
Sellafield nuclear reprocessing plant	1720	[32]
La Hague nuclear reprocessing plant	154	[32]
Global weapons fallout (1940s–1970s)	140	[27]
Nuclear accident in Chernobyl	0.75	[34]
Estimated nuclear accident in Fukushima	>0.25	
Estimated medical application (^{99}Mo – $^{99\text{m}}\text{Tc}$ generator)	<0.02	
Estimated nuclear power plants	<0.01	

1.2. Environmental level of technetium-99

Because of the long half-life, ^{99}Tc can exist in the environment for a very long time. The concentration of ^{99}Tc in the environment depends not only on the contamination level of the sampling area, but also on the sample type. In areas without direct contamination, the level of ^{99}Tc is normally low. The accumulated deposition from weapons fallout is in the order of 500 mBq m^{-2} [35] and a ^{99}Tc concentration of $4\text{--}88\text{ mBq kg}^{-1}$ was reported in Japanese soils in 2002 [36]. In precipitation, the concentration of ^{99}Tc ranges from 20 to $60\text{ }\mu\text{Bq L}^{-1}$, while in seawater it is only some few $\mu\text{Bq L}^{-1}$ [37–39]. However, ^{99}Tc concentrations of 0.4 Bq kg^{-1} (dry mass) in *Fucus vesiculosus* from north-western Spain [40], and of 0.1 Bq kg^{-1} (dry mass) from southern Spain have been observed, in areas where no direct ^{99}Tc contamination was reported [41]. This is attributed to the very high enrichment of ^{99}Tc in seaweed (10^5 in *Fucus*).

Because of anthropogenic nuclear activities, the levels of ^{99}Tc in some areas, especially in the contaminated environment near the sources, are relative high. Table 3 summaries the ^{99}Tc level in samples from some specific contaminated areas as well as corresponding background areas. As the major sources of ^{99}Tc , Sellafield and La Hague reprocessing plants discharge ^{99}Tc directly into Irish Sea and English Channel respectively. This ^{99}Tc is then transported to the North Sea and further northwards through the Norwegian Sea to the Arctic and Greenland Sea. Seawater in these areas is contaminated and the concentration of ^{99}Tc is enhanced. About 500 mBq L^{-1} of ^{99}Tc has been measured in seawater collected in an area close to the discharge point at Sellafield reprocessing plant in the Irish Sea [42], and a concentration of 60 mBq L^{-1} has been measured in seawater from the open Irish Sea in 1996–1997 [43]. The level of ^{99}Tc then decreases below 20 mBq L^{-1} after 1998 [26]. The discharge of radioactive wastes from La Hague reprocessing plant also increases the level of ^{99}Tc in marine waters. A concentration of $5\text{--}21\text{ mBq L}^{-1}$ in coastal seawater from the English Channel has been reported several decades ago [44]. In the North Sea water, concentrations of ^{99}Tc range from 15 to 75 mBq L^{-1} in the early 1980s [45]. A slightly lower value of 9 mBq L^{-1} has been measured in Norwegian coastal water in 1996–1997 [46]. The influence of reprocessing discharges at Sellafield and La Hague has also been observed at the Greenland coasts and in the Arctic environment. A concentration of $0.01\text{--}0.3\text{ mBq L}^{-1}$ of ^{99}Tc in seawater from the Greenland Sea was detected in our laboratory during the years 2000–2008 (unpublished data), and 0.07 mBq L^{-1} in the Arctic seawater [47]. This is about one order of magnitude higher than that in the background area [37–39].

The concentration of ^{99}Tc in aquatic plants and animals is also higher in contaminated environments than in uncontaminated areas. For example, a concentration of ^{99}Tc up to 10 Bq g^{-1} has been observed in *Fucus vesiculosus* from the Irish Sea during the operation of the Enhanced Actinide Removal Plant (EARP) at Sellafield, because of the increased discharges of ^{99}Tc to the marine system [43]. A long time measurement series of ^{99}Tc in our lab shows that the level of ^{99}Tc ranged from 1 to 40 mBq g^{-1} in *Fucus vesiculosus*

(dry mass) at the coast of Greenland during the years of 1991–2003 (unpublished data). Shellfish like lobster expresses an ability for accumulation of ^{99}Tc . The activity concentration of ^{99}Tc in lobsters landed at the Saltee Islands in the southeast coast of Ireland in 1997 was observed to be 1.57 mBq g^{-1} (wet weight), where a slight contamination of ^{99}Tc from the Sellafield reprocessing plant was reported. However, much higher values of $48\text{--}280\text{ mBq g}^{-1}$ (wet weight) were observed in the lobster landed at the east coast of Ireland during the years of 1997–1999, reflecting a strong contamination of ^{99}Tc by the discharges from the Sellafield reprocessing plant [43]. In Denmark, our laboratory has measured ^{99}Tc concentrations of $20\text{--}60\text{ mBq g}^{-1}$ (dry weight) in lobsters from Danish waters in 1998. A recent investigation showed that concentrations of ^{99}Tc in lobsters are still high in contaminated environments: 250 mBq g^{-1} (fresh) in the Sellafield coast area and $14\text{--}30\text{ mBq g}^{-1}$ (fresh) in the coastal area of Northern Ireland [32].

The ^{99}Tc level in the atmosphere is relatively low. Concentrations from 0.001 to 0.1 mBq L^{-1} have been reported in rainwater collected in southern Spain during the years 1984–1987 [48]. A similar value of 0.05 mBq L^{-1} on average has been reported in rainwater collected from United States in 1967 [49]. Compared with the atmosphere, the level of ^{99}Tc in soil and sediment, especially in samples from contaminated areas, are high. A concentration of 14.9 mBq g^{-1} ^{99}Tc has been reported in sediments from the Irish Sea close to Sellafield [50], which is several orders of magnitude higher than the level of ^{99}Tc in normal sediment samples ($<10\text{ }\mu\text{Bq g}^{-1}$ dry sample). ^{99}Tc concentrations of $1\text{--}15\text{ mBq g}^{-1}$ in soil and $0.2\text{--}6\text{ mBq g}^{-1}$ in vegetation samples collected in the 30-km zone around Chernobyl have been reported [12]. However, in uncontaminated environments, ^{99}Tc concentrations of $0.006\text{--}0.1\text{ mBq g}^{-1}$ have been observed in paddy field soil (dry weight) [51].

1.3. Physicochemical properties of technetium and its environmental behaviours

Technetium metal is silvery-gray colored and tarnishes slowly in moist air. It dissolves in HNO_3 , aqua regia and concentrated H_2SO_4 , but is not soluble in any strength of HCl solution [52]. Tc can exist in different oxidation states in aqueous solutions including Tc(II) , Tc(IV) , Tc(V) , Tc(VI) and Tc(VII) , and each of them can be prepared under appropriate conditions. In environmental conditions, Tc primarily exists in two oxidation states Tc(IV) and Tc(VII) . Under oxidizing conditions, Tc exists as pertechnetate ion (TcO_4^-) in aqueous solution or as volatile Tc_2O_7 in the absence of water. Tc_2O_7 melts at 119.5°C and boils at 311°C , it is very hygroscopic, and dissolves in water to form HTcO_4 [53]. In reductive conditions, Tc(IV) is the most stable oxidation state and strongly hydrolyzes in aqueous solutions and is very stable as TcO_2 in the absence of water [54]. In addition, various complexes of Tc(IV) can be formed in the presence of organic or inorganic ligands such as carbonate, EDTA, citrate and natural humic substances [55–58].

TcO_4^- is stable in water over a wide pH range in the absence of reducing substances. Because of the weak sorption of TcO_4^- in various environmental media, Tc is considered to be one of the most mobile radionuclides in the environment. Strong reductive reagents such as sulphite, meta-bisulphite, hydrazine or ascorbic acid are often applied to reduce TcO_4^- to lower oxidation states such as Tc(IV) [5,6,38,59]. Conversely, strong oxidants like bromine water, hydrogen peroxide, alkaline peroxide, hypochlorite, or persulphate, are employed to rapidly oxidize the lower oxidation state of Tc to TcO_4^- [60–63].

The behaviour of ^{99}Tc in environment is complex and controlled by physical, chemical and biological processes. ^{99}Tc has been released from the nuclear reprocessing plants mostly as TcO_4^- , which has a high mobility and easily enters into ecosystem [64].

Table 3
Environmental concentrations of ^{99}Tc arising from different source terms.

Source	Location	Sample	Concentration of ^{99}Tc	Reference
Chernobyl accident	30-km zone around the Chernobyl nuclear power plant	Soil	1–15 mBq g^{-1}	[12]
	30-km zone around the Chernobyl nuclear power plant	Vegetation	0.2–6 mBq g^{-1}	[12]
Nuclear fuel reprocessing plants	Areas near Sellafield reprocessing plant	Cabbage	13 mBq g^{-1} (fresh)	[32]
	Areas near Sellafield reprocessing plant	Leek	1.4 mBq g^{-1} (fresh)	[32]
	Areas near Sellafield reprocessing plant	Onions	2.3 mBq g^{-1} (fresh)	[32]
	Areas near Sellafield reprocessing plant	Potatoes	5.1 mBq g^{-1} (fresh)	[32]
	Areas near Sellafield reprocessing plant	Lobster	250 mBq g^{-1} (fresh)	[32]
	Areas near Sellafield reprocessing plant	Soil	820 mBq g^{-1} (fresh)	[32]
	Open Irish Sea (1996–1997)	Seawater	60 mBq L^{-1}	[43]
	Near Balbriggan in Irish Sea (1988–1993)	Seaweed	$340 \pm 80 \text{ mBq g}^{-1}$	[43]
	Near Capenhurst in Irish Sea	Sediment	18–450 mBq g^{-1}	[32]
	English Channel	Seawater	5–21 mBq L^{-1}	[44]
	North Sea (in early 1980s)	Seawater	15–75 mBq L^{-1}	[45]
	The Arctic	Seawater	0.07 mBq L^{-1}	[47]
	Japan Sea	Seawater	1–10 $\mu\text{Bq L}^{-1}$	[38]
	Japan	Soil	4–88 mBq kg^{-1}	[36]
Weapons fallout (Background)	Northwest and south Spain	Seaweed	0.1–0.4 mBq g^{-1} (dry mass)	[40]

After the discharge of ^{99}Tc into the seawater, it can be dispersed by sea currents or concentrated by seaweeds or marine animals. Because of the high mobility of TcO_4^- , ^{99}Tc is transported by sea currents over long distances from the discharge points (e.g., Sellafield and La Hague). It is therefore widely used as an oceanographic tracer to track seawater movement and coastal pollution [65]. ^{99}Tc was also released and dispersed into air from the atmospheric nuclear weapons testing or nuclear accidents such as Chernobyl and Fukushima accidents. The uptake in aquatic plants and marine animals is the most important way for ^{99}Tc to enter food chains. Seaweed can highly concentrate ^{99}Tc . The possible mechanism is that TcO_4^- in seawater is first taken up through foliar absorption, and then reduced to Tc(IV) in the chloroplast. The reduced Tc is afterwards absorbed or complexed with organic ligands in seaweed and fixed [66]. ^{99}Tc can also be taken up by terrestrial plants from soil and then concentrated by herbivores through ingestion of plants. Aquatic animals like shellfish, especially lobster, expresses a high ability to concentrate ^{99}Tc [43]. After death and decay of plants or animals, ^{99}Tc might accumulate in sediments or enter into water,

soil and other media. Fig. 3 shows the possible transport processes of ^{99}Tc in ecosystems.

2. Analytical methods for determination of technetium-99 in the environment

So far, a large number of analytical methods have been developed and applied for determination of ^{99}Tc in various environmental samples, such as soil, sediment, seaweed, seawater, groundwater, surface water and nuclear waste [4–9,14–16,18–21]. Table 4 summarizes the reported methods for ^{99}Tc determination along with typical recoveries and detection limits. In general, all of these methods are implemented in four steps: (1) sample pre-treatment, (2) chemical separation and purification, (3) source preparation and (4) ^{99}Tc measurement. Fig. 4 shows a flow chart of the analytical procedure for ^{99}Tc . A detailed discussion on the analytical procedures is presented below.

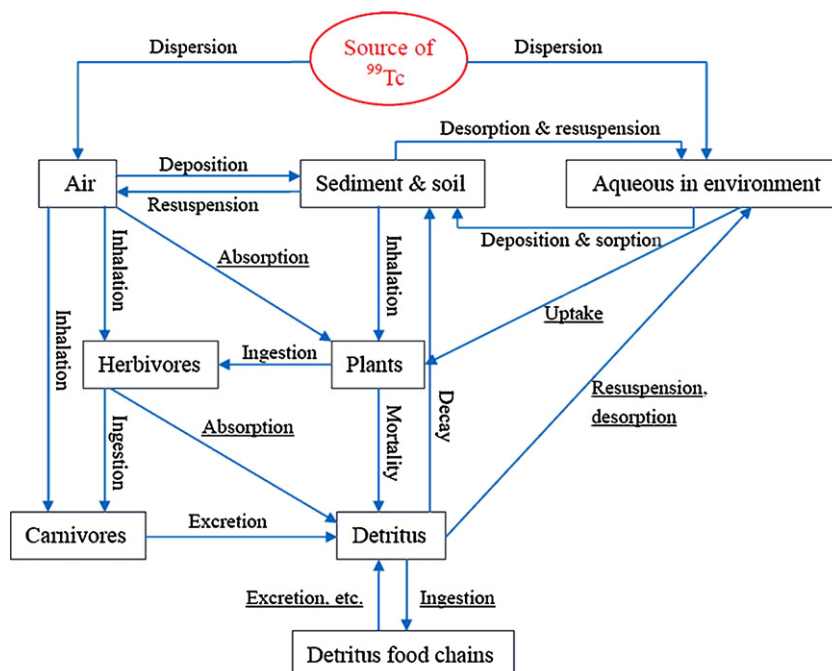


Fig. 3. Possible transport processes of ^{99}Tc in ecosystems. Modified from Wigley [68].

Table 4A summary of reported analytical methods for the determination of ^{99}Tc in different environmental samples.

Sample	Sample size	Yield monitor	Separation and purification	Recovery	Determination method	Detection limit of ^{99}Tc	Reference
Seawater	200–400 L	$^{99\text{m}}\text{Tc}$	Anion exchange with AG1-X4; Solvent extraction with $\text{TiOAc}/\text{xylene}$	70%	Gas flow GM counter	$4.68 \times 10^{-15} \text{ g L}^{-1}$	[6]
Radioactive waste	1–10 g	$^{99\text{m}}\text{Tc}$	Co-precipitation with $\text{Fe}(\text{OH})_2$; Solvent extraction with CHCl_3	>90%	Proportional counter	$1.01 \times 10^{-11} \text{ g g}^{-1}$	[59]
Seaweed, lobster and sediment	10 g	$^{99\text{m}}\text{Tc}$	Anion exchange with 1×8 ; Solvent extraction with $\text{TiOAc}/\text{xylene}$	70–95%	LSC	$1.65 \times 10^{-12} \text{ g g}^{-1}$	[8]
Aqueous sample	1 L	^{97}Tc	Solid phase extraction with TEVA	>90%	ID-ICP-MS	$1.87 \times 10^{-11} \text{ g L}^{-1}$	[25]
Soil	3–6 g	Re	On-line flow injection separation with extraction chromatography using TEVA	62–73%	FI-HR-ICP-MS	$7.80 \times 10^{-11} \text{ g L}^{-1}$	[91]
Seaweed, sediment	10 g	$^{95\text{m}}\text{Tc}$	Recrystallisation; Solid phase extraction with TEVA	50–90%	ICP-MS	$1.56 \times 10^{-12} \text{ g g}^{-1}$	[11]
Water sample	500 L	$^{95\text{m}}\text{Tc}$	Co-precipitation with $\text{Fe}(\text{OH})_2$; Solid phase extraction with TEVA	50–80%	ICP-MS	$4.68 \times 10^{-14} \text{ g L}^{-1}$	[92]
Contaminated water sample	–	$^{99\text{m}}\text{Tc}$	Solid phase extraction with TEVA	85–98%	ETV-ICP-MS	$(4.99\text{--}9.88) \times 10^{-10} \text{ g L}^{-1}$	[113]
Soil and sediment	1–20 g	$^{95\text{m}}\text{Tc}$	Solvent extraction; Anion exchange with Dowex 1-X8	84–92%	HR-ICP-MS	$2.50 \times 10^{-13} \text{ g}$	[102]
Dry-up deposition sample	3 g	$^{95\text{m}}\text{Tc}$	Volatilization; Solvent extraction with cyclohexanone	77%	ICP-MS	–	[76]
Soil and sediment	10 g	Re	Anion exchange with Dowex 1-X8; Solid phase extraction with TEVA	–	ICP-MS	–	[62]
Seawater	14 mL	Re	Anion exchange with IRA-400 resin	>85%	ICP-MS	$4.68 \times 10^{-11} \text{ g L}^{-1}$	[42]
Seawater	0.25–5 L	$^{95\text{m}}\text{Tc}$	Solid phase extraction with TEVA	–	AMS	$\sim 3.9 \times 10^{-15} \text{ g}$	[14]
Soil sample	0.25 g	Re	Solid phase extraction with TEVA	>93%	FI-ICP-MS	$2.0 \times 10^{-11} \text{ g g}^{-1}$	[133]
Vegetation	25 g	^{95}Tc	Anion exchange with Dowex 1-X8; Solvent extraction with cyclohexanone	80%	NAA	$9.36 \times 10^{-12} \text{ g g}^{-1}$	[84]
Water sample	5–30 L	$^{95\text{m}}\text{Tc}$	Solvent extraction with $\text{TiOAc}/\text{xylene}$; Anion exchange with Dowex 1-X8	$65 \pm 15\%$	ICP-MS	$3.93 \times 10^{-9} \text{ g L}^{-1}$	[98]
Drinking water	1–2 L	Re	Solvent extraction with $\text{TiOAc}/\text{xylene}$; Solid phase extraction with TEVA	$102 \pm 6.5\%$	ICP-MS	$1.01 \times 10^{-12} \text{ g L}^{-1}$	[9]
Tank waste sample	1 mL	$^{95\text{m}}\text{Tc}$	On-line sequential injection separation with TEVA	–	SI-LSC	$2.03 \times 10^{-9} \text{ g}$	[132]
Soil, Biota and sediment	15–100 g	$^{99\text{m}}\text{Tc}$	Co-precipitation with $\text{Fe}(\text{OH})_2$; Solvent extraction with TBP	50–80%	Gas flow GM counter	$2.18 \times 10^{-12} \text{ g}$	[5]
Soil sample	50 g	$^{95\text{m}}\text{Tc}$	Volatilization; Solid phase extraction with TEVA	62–73%	ICP-MS	$1.72 \times 10^{-15} \text{ g g}^{-1}$	[94]
Geological samples	2.5–15 g	^{97}Tc	Solvent extraction with CHCl_3 ; Anion exchange with AG MP 1 X8	10–80%	TIMS	$1.09 \times 10^{-14} \text{ g}$	[17]

2.1. Chemical yield tracers for determination of technetium-99

As mentioned above, the concentration of ^{99}Tc in environmental samples is normally very low. An extensive chemical separation has to be implemented for concentrating ^{99}Tc from samples and removal of matrix components and interferences. The measurement of chemical yield of ^{99}Tc during the chemical separation is a key issue for obtaining accurate analytical results. The yield tracer can also be used in mass spectrometric measurement of ^{99}Tc as an internal standard or isotopic addition standard, which can eliminate and/or reduce the analytical error induced by instability of the instrument during the measurement.

Several yield tracers have been used in the determination of ^{99}Tc , including isotopic tracers, such as $^{95\text{m}}\text{Tc}$, $^{97\text{m}}\text{Tc}$, ^{97}Tc , ^{98}Tc and $^{99\text{m}}\text{Tc}$, and non-isotopic tracers such as enriched stable isotopes of rhenium (^{185}Re or ^{187}Re) or natural rhenium (Re). Table 5 lists all these yield tracers and their nuclear/physical properties. $^{95\text{m}}\text{Tc}$ decays mainly by electron capture, and a small fraction by positron emission (0.44%), with emission of γ rays of energies 204.1 keV (63.3%), 582.1 keV (30.0%), 835.1 keV (26.6%), 786.2 keV (8.7%), and 820.6 keV (4.7%). It is therefore easily measured by γ -spectrometry. The half-life (61.0 d) makes $^{95\text{m}}\text{Tc}$ a useful tracer for days-to-weeks sample pre-treatment especially for field experiments. Meanwhile the large difference in mass compared with ^{99}Tc means that the isobaric interference can be avoided in the determination of ^{99}Tc by ICP-MS. However, it has been reported that the commercial $^{95\text{m}}\text{Tc}$ solution often contains detectable amounts of ^{99}Tc , which will increase the blank level, and increase the detection limit for

low level ^{99}Tc measurement [67]. In addition, radioactive $^{95\text{m}}\text{Tc}$ interferes in the measurement of ^{99}Tc by beta counting, and due to its 61 d half life, $^{95\text{m}}\text{Tc}$ needs to decay away over several months before measurement of ^{99}Tc by radiometric methods, especially for β counting using GM counter. Anyway, $^{95\text{m}}\text{Tc}$ has been a popular yield tracer in the determination of ^{99}Tc in the early days. $^{97\text{m}}\text{Tc}$, as a meta-isomer of ^{97}Tc , decays to ^{97}Tc by isomeric transition and a very small fraction (<0.34%) by electron capture. Although $^{97\text{m}}\text{Tc}$ emits soft γ rays (96.5 keV), the intensity of these γ rays is very low (0.31%), which makes it unsuitable as a yield tracer for determination of ^{99}Tc . As a result, its application as a tracer is very limited. $^{95\text{m}}\text{Tc}$ and $^{97\text{m}}\text{Tc}$ can be produced by cyclotron via $^{95}\text{Mo}(\text{p}, \text{n})^{95\text{m}}\text{Tc}$ and $^{97}\text{Tc}(\text{n}, \text{n}')^{97\text{m}}\text{Tc}$ reactions. Neither $^{95\text{m}}\text{Tc}$ nor $^{97\text{m}}\text{Tc}$ can be used as internal standard in ICP-MS because of their relatively short half lives. ^{97}Tc is a long-lived radioisotope of Tc ($t_{1/2} = 2.6 \times 10^6 \text{ y}$), and decays by electron capture without any γ ray emission. Therefore it is difficult to measure by radiometric methods. ^{98}Tc is also a long-lived radioisotope of Tc ($t_{1/2} = 4.2 \times 10^6 \text{ y}$), which decays by emitting β particles of maximum energy of 398.2 keV, with γ rays of 652.4 keV (100%) and 745.4 keV (100%). It is difficult to isolate from ^{99}Tc in the radiometric measurement of ^{99}Tc . Therefore it seriously interferes in the measurement of ^{99}Tc in β counting using GM counter as well as liquid scintillation counter. However, ^{97}Tc and ^{98}Tc are ideal yield tracers for the determination of ^{99}Tc when mass spectrometric methods are used, because of their long half-lives, and similar amount of mass as ^{99}Tc in the solution. The drawbacks of ^{97}Tc and ^{98}Tc as yield tracers are their isotopic purity and availability. A pure ^{97}Tc or ^{98}Tc source is difficult to obtain. Normally

Table 5
Major yield tracers for the determination of ^{99}Tc .

Tracer	Half-life/abundance	Decay mode	Detection method	Main production mode	Major disadvantages
$^{95\text{m}}\text{Tc}$	61.0 d	EC/IT	γ -Spectrometry	$^{95}\text{Mo}(\text{p}, \text{n})^{95\text{m}}\text{Tc}$	Spectral interference/difficult available
$^{97\text{m}}\text{Tc}$	90.1 d	IT	γ -Spectrometry	$^{97}\text{Mo}(\text{p}, \text{n})^{97\text{m}}\text{Tc}$	Spectral interference/difficult available
^{97}Tc	2.6×10^6 y	β^-	ICP-MS	$^{95}\text{Mo}(\alpha, 2\text{n})^{97}\text{Ru}(\beta^-)^{97}\text{Tc}$	Difficult available/high cost
^{98}Tc	4.2×10^6 y	β^-	ICP-MS	$^{98}\text{Mo}(\text{p}, \text{n})^{98}\text{Tc}$	Difficult available/high cost
$^{99\text{m}}\text{Tc}$	6.01 h	IT	γ -Spectrometry	$^{99}\text{Mo}(\beta^-)^{99\text{m}}\text{Tc}$	Short half-life
^{185}Re	37.4%	Stable	ICP-MS	Natural	Difference in chemical properties with Tc
^{187}Re	62.6%	Stable	ICP-MS	Natural	Difference in chemical properties with Tc

EC, electron capture; IT, isomeric transition.

the products contain both ^{97}Tc and ^{98}Tc , as well as a small amount of ^{99}Tc [68]. In addition, these two isotopes are still not commercial available, which limits their application in routine analysis. $^{99\text{m}}\text{Tc}$ is a metastable nuclear isomer of ^{99}Tc , with a short half life of only 6.1 h. It de-excites to ^{99}Tc by emitting γ ray of 140.5 keV. $^{99\text{m}}\text{Tc}$ is normally obtained through decay of ^{99}Mo using ^{99}Mo – $^{99\text{m}}\text{Tc}$ generator, where ^{99}Mo can be produced by neutron induced fission of ^{235}U , and neutron activation of ^{98}Mo . Due to its wide application in nuclear medicine, $^{99\text{m}}\text{Tc}$ is the most easily available isotope of Tc. Therefore it has often been used as a yield tracer for the determination of ^{99}Tc [21,61]. After decay of $^{99\text{m}}\text{Tc}$ (usually one week), ^{99}Tc can be detected by radiometric methods or ICP-MS without obvious interference. Since $^{99\text{m}}\text{Tc}$ decays to ^{99}Tc by isomeric transition, the application of large amounts of $^{99\text{m}}\text{Tc}$ or aged $^{99\text{m}}\text{Tc}$ from the generator might cause a high blank level for determination of ^{99}Tc . Therefore newly in-grown $^{99\text{m}}\text{Tc}$ in the generator is used as yield tracer. $^{99\text{m}}\text{Tc}$ eluted from high radioactive ^{99}Mo – $^{99\text{m}}\text{Tc}$ generators used in hospitals (about 25 GBq) might contain a relatively significant amount of ^{99}Mo due to the radiolysis effect in the generator. This problem can be solved by purification of the $^{99\text{m}}\text{Tc}$ eluate using an alumina cartridge, and applying a reduced radioac-

tive ^{99}Mo – $^{99\text{m}}\text{Tc}$ generator (2–4 GBq) or a generator in which ^{99}Mo is produced by neutron activation of ^{98}Mo [63]. The above advantages, especially the easy availability of ^{99}Mo – $^{99\text{m}}\text{Tc}$ generators, make $^{99\text{m}}\text{Tc}$ the most frequently used chemical yield tracer for the determination of ^{99}Tc in recent years. Re is in the same group (VIIB) as Tc in the periodic table. Therefore the two elements have similar chemical properties. It is possible to use natural Re or enriched stable Re isotopes (^{185}Re or ^{187}Re) as non-isotopic yield tracer in the determination of ^{99}Tc [69–71]. In this case, Re has to be measured by non-radiometric methods. Therefore Re is often used as yield tracer when mass spectrometric methods are used for the measurement of ^{99}Tc , so that both ^{99}Tc and isotopes of Re can be simultaneously measured. Re isotopes can be used as an internal standard in the mass spectrometric measurement. Since they are not identical elements, Tc and Re might behave somewhat differently during the chemical separation. The main difference between Re and Tc is their redox potentials. The reduction of Re is more difficult than that of Tc [72], which might cause a significant fractionation between Re and Tc in the separation by co-precipitation of Tc after reducing Tc to Tc(IV) and forming hydroxide in alkali solution. Furthermore, the selectivity and

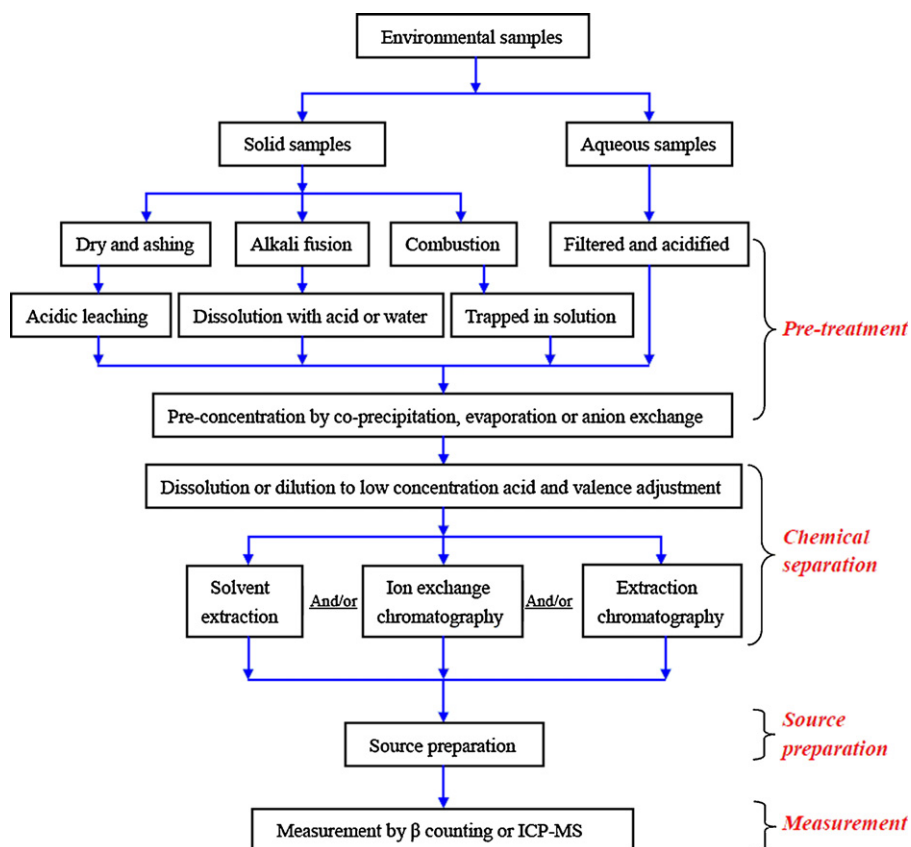


Fig. 4. Flow chart of an analytical procedure for determination of ^{99}Tc in environmental samples.

affinity of Re and Tc in the chromatographic resins are also not the same [73], resulting in a different elution curves for the two elements. All these issues have to be considered in the experimental design in order to obtain a reliable chemical yield during the chemical separation.

2.2. Sample pre-treatment

2.2.1. Aqueous samples

Aqueous samples (e.g., seawater, lake, river, rain, and ground water) are first filtered through appropriate filters to remove suspended particulate matter after sampling, and then acidified to pH 1–4 by concentrated acid using HCl [21,74,75], H₂SO₄ [6] or HNO₃ [49]. Since the concentration of ⁹⁹Tc in environmental water samples is normally very low, it requires sample pre-treatment to pre-concentrate ⁹⁹Tc. The enrichment of ⁹⁹Tc can be achieved by a few approaches, including evaporation [76], activated carbon adsorption [77], co-precipitation [21,38,40,59,75], and anion exchange chromatography [2,6] according to the volume and the salt content of the sample.

Evaporation is a simple method and can be adopted for samples of a relatively small volume and with low salt content such as rain/snow, river, lake water and some ground water. Because of the volatile property of Tc, it has been suggested that evaporation of water should be carried out in basic medium [4]. Some experiments [76] have shown no loss of ⁹⁹Tc during evaporation of water at 70–80 °C, and the adjustment of water to basic medium is not necessary when the temperature is kept under 90 °C [51]. However, when the solution is evaporated to dryness, some ⁹⁹Tc might be lost. The reason for this is that ⁹⁹Tc can be converted to volatile Tc₂O₇ when the solution is dried and evaporate when the temperature rises. Our experiments show that the loss of ⁹⁹Tc is negligible if the sample solution is not evaporated to dryness (more than 0.5 mL solution left) even in high concentration of nitric acid. Although the evaporation method is simple it appears unpractical for large volume samples with high salt content, like seawater. In this case, anion exchange chromatography, co-precipitation or activated carbon adsorption can be utilized to pre-concentrate ⁹⁹Tc from sample matrices.

Based on the very high affinity of TcO₄[−] to anion exchange resin, Chen et al. [6] have described an ion exchange method to separate and pre-concentrate ⁹⁹Tc from up to 200 L fresh seawater employing strong basic anion exchange resin Bio-Rad AG1-×4 in a column with a diameter of 2.5 cm and a height of 40 cm. After converting all Tc in the water to Tc(VII) by H₂O₂ in acidic medium, the seawater sample is loaded to columns at the flow rate of 150–200 mL min^{−1}, and a chemical yield of ⁹⁹Tc of more than 90% is obtained. This method has been successfully applied for routine analysis of seawater samples for ⁹⁹Tc in our laboratory at Risø, Denmark. The key issue in this procedure is the conversion of ⁹⁹Tc to the TcO₄[−] form, because other forms of Tc could not be sufficiently retained by the anion exchange column. It should be mentioned that the formation of colloids or even larger suspended matters in long term storage of the water sample may cause a problem in the column separation and pre-concentration. The suspended materials in water will be accumulated on the top of the column and cause failure of the separation due to blocking of the column. The colloid formed in the water might coat the surface of the exchange resin, resulting in a low chemical yield of ⁹⁹Tc in this separation procedure. The long time of operation is the main drawback of this method for pre-concentration of ⁹⁹Tc. For a 200 L water sample, this step takes about 20 h.

Pre-concentration by co-precipitation is based on insolubility of low oxidation states of Tc, such as TcO₂, and their strong sorption to particles or precipitate formed in the solution. In this method, reductant, such as FeSO₄ or sulphite, and carrier, such

as FeCl₃·6H₂O, are firstly added to the water, and then NH₃·H₂O or NaOH is added to adjust pH to 9 to form Fe(OH)₂ precipitation, which carries the formed TcO₂ and separates it from the water matrix. This method has been successfully applied to pre-concentrate ⁹⁹Tc from 1 to 100 L seawater and rain water samples, and chemical yield of 50–80% depending on the volume of the sample has been reported [5]. Other carrier/reductant, such as CuS, has also been used for this purpose [78]. Comparing with the anion exchange method, the co-precipitation method is relatively rapid and the problems with column blocking can be avoided when analyzing sample after a long storage time. The most attractive advantage of this method is that it is very suitable for the pre-concentration of ⁹⁹Tc in the field (or on board a sampling vessel), which significantly reduces the problem of transport of large volumes of water samples. However, the chemical yield of ⁹⁹Tc in the co-precipitation process decreases with the increase in sample volume. Meanwhile a large amount of precipitate formed in the treatment of large volumes of sample will cause other problems in the following separation and purification steps.

Activated carbon adsorption has also been reported for pre-concentration of ⁹⁹Tc from water samples [77]. Because of the large specific surface area (400–1600 m² g^{−1}), ⁹⁹Tc can be effectively adsorbed from water samples using activated carbon. It has been reported that ⁹⁹Tc can be rapidly (5 L min^{−1}) concentrated from very large volume (several hundred liters) of environmental waters on commercial cartridge filters impregnated with activated carbon [77]. The adsorption efficiency of ⁹⁹Tc can be enhanced when ⁹⁹Tc is reduced to the low oxidation state of Tc(IV). However, if organic compounds exist in the sample, the sorption efficiency of ⁹⁹Tc will obviously be reduced; furthermore, the adsorbed ⁹⁹Tc needs to be removed from cartridge filters to aqueous solution for further separation. An additional ashing step might be added for this purpose, which will prolong the analysis time. Compared with the co-precipitation and anion exchange chromatography methods, activated carbon sorption is not commonly used as a method for ⁹⁹Tc pre-concentration.

2.2.2. Solid samples

2.2.2.1. Initial pre-treatment of samples. For analysis of solid samples (e.g., soil, seaweed, and sediment), the impurity materials such as stones and roots of vegetations are first removed. A sufficient amount of samples is then dried at 60–105 °C, ground, and sieved to get a homogeneous and representative sample for analysis [79,80]. Afterwards, organic matters in solid samples are decomposed by incinerating in muffle furnaces [8,11,12,21,39,81,82]. This is a very critical step in the analysis of solid samples for ⁹⁹Tc, because incomplete decomposition of organic matters and volatile loss of ⁹⁹Tc in this stage will cause an insufficient leaching of ⁹⁹Tc from the samples and poor yield of ⁹⁹Tc. Some reports suggest that ⁹⁹Tc losses occur at a temperature around 550 °C [8,83], whereas others reported an insignificant loss of ⁹⁹Tc even at as much as 800 °C [84,85]. It has been reported that the loss of ⁹⁹Tc can be reduced if the samples are wetted with concentrated HCl before ashing [5]. This is explained by the reduction of Tc to Tc(IV) in high concentration of HCl, and the stability of the Tc(IV) oxidation state compared with high oxidation states of Tc. Wigley et al. reported that NH₃·H₂O is more suitable than HCl as the wet reagent to prevent the loss of ⁹⁹Tc in the ashing step [8], because the amount of volatile HTcO₄ can be limited by the addition of NH₃·H₂O before ashing. However, some investigations indicate that solid samples such as seaweed treated with NH₃·H₂O did not show any difference in the chemical yield compared with untreated samples at an ashing temperature below 750 °C [11]. To avoid the problem of ⁹⁹Tc loss during incineration at high temperature, a wet ashing method using concentrated H₂SO₄ carbonization and HNO₃ digestion has been applied to decompose organic matter for

analyzing seaweed [86]. Our recent experiment using ^{99m}Tc tracer showed that ashing of soil, sediment and seaweed samples at less than 700°C does not cause any loss of ^{99}Tc . Yield tracer is normally added after pre-treatment but before ashing of samples in order to estimate the chemical yield of ^{99}Tc during the analytical procedure.

2.2.2.2. Separation of technetium from sample matrixes. Before further chemical separation, ^{99}Tc should be released from the sample matrix into solution. Two common techniques for releasing ^{99}Tc from solid samples after ashing are acid leaching [8,11,12,82] and alkali fusion [17,87–89]. Concentrated HNO_3 [6,90], $8\text{ mol L}^{-1}\text{ HNO}_3$ [8,82], $4\text{ mol L}^{-1}\text{ HNO}_3$ [12,80,91], $6\text{ mol L}^{-1}\text{ HCl} + \text{H}_2\text{O}_2$ [83] and $3\text{ mol L}^{-1}\text{ HCl} + \text{H}_2\text{O}_2$ [92] have been utilized to leach ^{99}Tc from ashed samples under heating and reflux on a hot plate at $70\text{--}125^\circ\text{C}$. Wigley et al. [8] compared different leaching reagents ($8\text{ mol L}^{-1}\text{ HNO}_3$, diluted aqua regia, $8\text{ mol L}^{-1}\text{ HCl} + \text{H}_2\text{O}_2$, $4\text{ mol L}^{-1}\text{ HCl}$) for analysis of seaweed and sediment samples, and reported that $8\text{ mol L}^{-1}\text{ HNO}_3$ showed the highest yield of ^{99}Tc and 2 h are necessary to release ^{99}Tc from sample matrices. Diluted aqua regia and HCl are less efficient for leaching ^{99}Tc compared with HNO_3 but the reason is still unclear [8,93]. In fact, $8\text{ mol L}^{-1}\text{ HNO}_3$ is also the most often used reagent for leaching ^{99}Tc in the determination of ^{99}Tc in environmental samples. Acid leaching is not only the most commonly used method but is also suitable in connection with the pre-treatment of large samples. However, acid leaching might give rise to poor yield of ^{99}Tc when the organic matters are not decomposed completely before leaching. Addition of H_2O_2 in the acid digestion is therefore used to remove organic matters which were not completely decomposed before acid leaching. It should be mentioned that acid digestion/leaching can only release/remove ^{99}Tc absorbed on the surface of grains of solid samples. It is difficult to release ^{99}Tc , which remains inside the crystal of sample grains. Alkali fusion is a method for complete decomposition of solid samples, especially soil, sediment and rocks. A mixture of Na_2O_2 and carbonate-free NaOH was often used as fusion reagents for the decomposition of solid samples at $400\text{--}700^\circ\text{C}$ [17,88,89]. The fusion cake is dissolved with water or diluted acid solution prior to isolation of ^{99}Tc . This method can completely decompose the sample in short time (usually less than 1 h) and all of the ^{99}Tc would be released into solution. However, this method is not suitable for large samples, for example more than 10 g of soil or sediment, because 3–5 times amount of fusion reagents is normally used in this method, which will make the further treatment difficult when a large sample (for example 100 g soil or sediment) is analysed. Oxidizing combustion methods can also be used for releasing ^{99}Tc from solid samples [85,94]. This method is based on the volatility of Tc in oxidative medium and at high temperature. The solid sample is placed in a quartz boat which is inserted in a quartz tube in a furnace. The sample in the tube furnace is combusted under an oxygen stream at more than 1000°C for 3 h. The ^{99}Tc in sample is converted to volatile Tc_2O_7 and released from the sample, which is transported by the gas flow and trapped in alkaline solution or just water [85,94]. Compared with alkali fusion, the combustion method can be used to treat large samples using a big tube oven, and most of the matrix components as well as many interfering radionuclides and stable elements can be directly removed from the ^{99}Tc because of their lesser volatility in the combustion conditions. The chemical yield of ^{99}Tc with this method can easily exceed 95%. It has been reported that this method is difficult to use for analysis of large numbers of samples, because only one sample can be treated per day. In recent years, a multi-tubes combustion furnace has become commercially available. This furnace was initially designed for determination of ^{14}C and ^3H in solid waste, but with small modification, it can be used for ^{99}Tc (as well as for ^{129}I) determination in solid samples [95]. In this

Table 6The main potential interferences in the ^{99}Tc measurement.

Mass spectrometric methods [22]		Radiometric methods [68,83]	
Isobaric and molecular ions	Natural abundance (%)	Nuclides	β -max energy (keV)
^{98}Mo	24.1	^{60}Co	318.1
^{100}Mo	9.6	^{63}Ni	66.9
^{99}Ru	12.7	^{90}Sr (^{90}Y)	546.0(2280.1)
^{100}Ru	12.6	^{103}Ru	226.6
$^{98}\text{Mo}^1\text{H}$	24.1 (^{98}Mo)	^{106}Ru	39.6
$^{83}\text{Kr}^{16}\text{O}$	11.5 (^{83}Kr)	^{110m}Ag	529.8
$^{51}\text{V}^{16}\text{O}_3$	99.8 (^{51}V)	^{125}Sb	303.3
$^{59}\text{Co}^{40}\text{Ar}$	100 (^{59}Co)	^{137}Cs	514.0
$^{64}\text{Zn}^{35}\text{Cl}$	48.6 (^{64}Zn)	^{210}Pb	63.5

case, a large sample throughput is possible using the combustion method.

In summary, when organic matters in the solid samples are well incinerated and ^{99}Tc mainly exists on the surface of the sample grain, acid leaching is the most suitable and convenient method for release of ^{99}Tc from sample matrix. The alkali fusion method is more suitable for the samples in which ^{99}Tc might exist inside the crystal of sample grains, but difficult to use for large samples. Oxidizing combustion is a simple and efficient method for releasing ^{99}Tc from large samples, but a limitation is the low sample throughput.

2.3. Chemical separation and purification of technetium

The accuracy and precision of an analytical method for determination of ^{99}Tc rely on the level of removal of interferences and matrix components. Due to the low concentration of ^{99}Tc in the environment, a large sample is normally required for the analysis in order to obtain sufficient signal. The method adopted for the chemical separation of ^{99}Tc should be able not only to give a good decontamination from interferences but also to provide a high chemical yield of ^{99}Tc . For measurement of ^{99}Tc using radiometric methods, a thorough chemical separation of almost all other radionuclides from ^{99}Tc is required because of bad spectrometric resolution of the beta counting method [61,96]. For measurement of ^{99}Tc using mass spectrometric methods, for example ICP-MS, besides the interference of matrix elements, the interferences from isobaric and molecular ions in the mass of 99 is the main challenge [21,97]. Of these, the most important isobaric interferences are from $^{98}\text{Mo}^1\text{H}$ and ^{99}Ru . Table 6 shows the main potential interferences for the measurement of ^{99}Tc by radiometric and spectrometric methods. For separation and purification of ^{99}Tc , a variety of techniques have been used. The most common are co-precipitation, solvent extraction, ion exchange chromatography, extraction chromatography or a combination of two or more methods [5,8,62,82,89,98], these techniques are summarized and compared below.

2.3.1. Preconcentration of technetium by co-precipitation

Co-precipitation is a traditional method for radiochemical separation. For the precipitation of an element as its compound, the concentration of the precipitation reagent has to be high enough to exceed its solubility product (K_{sp}). Since the concentrations of ^{99}Tc in environmental samples are generally very low, and there is no stable isotope of Tc, its solubility products are seldom exceeded even with a saturated concentration of precipitation reagent in the sample solution. The co-precipitation technique is therefore often used to separate ^{99}Tc from sample matrix.

Under reductive conditions, ^{99}Tc mainly exists in the oxidation state of Tc(IV), which easily forms insoluble species of

$\text{TcO}_2 \cdot n\text{H}_2\text{O}$ in aqueous solution (usually in the form of $\text{TcO}_2 \cdot \text{H}_2\text{O}$) and can be co-precipitated by carrier such as $\text{Fe}(\text{OH})_2$ or FeS (CuS) from sample matrix. Two issues need to be considered during the co-precipitation: a suitable medium for co-precipitation and the reductive reagent. As discussed above, Tc is difficult to reduce to $\text{Tc}(\text{IV})$ in the HNO_3 medium but it can be realized easily in HCl solution. The sample solution is therefore converted to diluted HCl medium (e.g. 0.1 mol L^{-1} HCl) before the reduction and co-precipitation of Tc takes place. Many reductive reagents have been used for converting Tc to $\text{Tc}(\text{IV})$. In earlier studies, Holm et al. [5] compared the reductive abilities of SnCl_2 ($\text{Fe}(\text{OH})_2$ as co-precipitation reagent) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ for ^{99}Tc in 5 L seawater samples. It was reported that both SnCl_2 (0.5 g L^{-1}) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.7 g L^{-1}) can convert Tc to $\text{Tc}(\text{IV})$ and ^{99}Tc is efficiently co-precipitated with $\text{Fe}(\text{OH})_2$. However, the dissolution of the co-precipitated Tc by re-oxidation of $\text{Tc}(\text{IV})$ to $\text{Tc}(\text{VII})$ is difficult if the SnCl_2 is used as reductive reagent and the mechanism is still not clear. Comparing with SnCl_2 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ shows better characteristics for Tc separation by co-precipitation, and it is not necessary to add additional iron compounds such as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to form $\text{Fe}(\text{OH})_2$ precipitation. In fact, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ has often been utilized to reduce Tc during co-precipitation separation of ^{99}Tc in liquid samples as well as from the leachate of seaweed [40]. However, for soil and sediment, it is not very sensible to choose $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as the reductive reagent because of a large amount of iron existing in these types of samples. In addition, a large amount of precipitate will be produced if $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is used, which might decrease the chemical yield of ^{99}Tc during the separation of Tc from iron by converting $\text{Tc}(\text{IV})$ to soluble TcO_4^- and removal of iron by precipitation of $\text{Fe}(\text{OH})_3$. This might be attributed to the fact that some TcO_4^- can be enwrapped in $\text{Fe}(\text{OH})_3$ precipitate although Tc has been converted to $\text{Tc}(\text{VII})$. $\text{K}_2\text{S}_2\text{O}_5$ (KHSO_3 form in solution) is another reductive reagent which can be used in the reduction of TcO_4^- to $\text{Tc}(\text{IV})$. It has been reported that TcO_4^- can be easily reduced to $\text{Tc}(\text{IV})$ by $\text{K}_2\text{S}_2\text{O}_5$, and the formed $\text{Tc}(\text{IV})$ in the co-precipitate can be transferred to solution by oxidizing it to TcO_4^- again [74]. In fact, $\text{K}_2\text{S}_2\text{O}_5$ has been widely applied in many analytical procedures of ^{99}Tc for the reduction of Tc to low oxidation state [13,61].

After the pre-concentration of ^{99}Tc by co-precipitation, it is necessary to transfer ^{99}Tc into aqueous solution for further separation, and this can be accomplished by oxidizing $\text{Tc}(\text{IV})$ to TcO_4^- based on the high solubility of TcO_4^- in aqueous solution. Different oxidative reagents like H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$ have been added after dissolving the co-precipitate of Tc with $\text{Fe}(\text{OH})_2$ in acid to oxidize $\text{Tc}(\text{IV})$ to $\text{Tc}(\text{VII})$; Fe as well as other transition metals, actinides and lanthanides are then removed effectively through $\text{Fe}(\text{OH})_3$ co-precipitation, while leaving TcO_4^- in solution [62].

Co-precipitation is a very simple method and can be used to separate ^{99}Tc from sample matrix effectively. A batch of samples (8–12) is treated in a short time and no other chemical waste is produced during the process. However, a low recovery of ^{99}Tc might be the result when analyzing a large volume of water (for example 200 L seawater). In addition, the decontamination factor of this method alone is normally not very high for most interference. In practice, the co-precipitation technique is often used to pre-concentrate and separate Tc from the major matrix components of large samples; it is common to combine with other techniques like solvent extraction, anion exchange or extraction chromatography for ^{99}Tc separation and purification.

2.3.2. Solvent extraction

Several extractants like tri-iso-octylamine (TiOA), tributylphosphate (TBP) and cyclohexanone have been applied for separation of ^{99}Tc from other radionuclides and matrix components.

TiOA is the most common extractant applied for the separation of ^{99}Tc [4,8,9,74,99]. This is based on the formation of a neutral complex of TcO_4^- with TiOA in low concentration of acid. It has been reported that ^{99}Tc can be easily extracted by 5% TiOA/xylene (ratio of volume) from 0.5 mol L^{-1} H_2SO_4 solution, and ^{99}Tc in the organic phase can be back-extracted by low concentration NaOH solution [4]. As the main interference in ^{99}Tc measurement, Ru can be removed effectively in this step. Reported distribution coefficients for Ru and ^{99}Tc between 5% TiOA/xylene and 0.5 mol L^{-1} H_2SO_4 solution are 3.8×10^{-3} and 2.5×10^3 , respectively [6]. This feature can be explained as that in low concentration H_2SO_4 , Tc is oxidized to TcO_4^- , but Ru is kept in a low oxidation state, which cannot be extracted by 5% TiOA/xylene if a mild oxidizing reagent such as H_2O_2 is used. It has been observed that ^{99}Tc cannot be separated from Ru by extraction with 5% TiOA/xylene in H_2SO_4 solution if a strong oxidizing reagent such as NaClO is used [6]. In this case, Tc and Ru are oxidized to TcO_4^- and RuO_4^- respectively, and both of them are extracted by TiOA. As another trioctyl amine, Trioctylamine (TOA) has also been applied to extract ^{99}Tc for separation of it from other interfering cations. H_2SO_4 medium is often used in the extraction of Tc using TiOA/xylene although this is not effective for Mo decontamination.

TBP is a conventional extractant extensively used in plutonium-uranium extraction in PUREX process in the spent fuel reprocessing. It can also be used to separate ^{99}Tc from other interferences [2,21,93,99]. This is based on the fact that in acid medium, TcO_4^- combines with H^+ or H_3O^+ to form neutral molecular HTcO_4 or $\text{HTcO}_4(\text{H}_2\text{O})$, which can form a complex with TBP to be extracted [100]. The choice of a suitable medium for TBP extraction is very critical. Relatively low concentration of HNO_3 or H_2SO_4 is often utilized during ^{99}Tc extraction. ^{99}Tc is easily extracted by TBP in $0.1\text{--}2 \text{ mol L}^{-1}$ HNO_3 solution, and chemical yield of ^{99}Tc is not high in other concentrations of HNO_3 [101]. This can be explained as that in low concentration of HNO_3 , HTcO_4 is not easily formed, while in higher concentration of HNO_3 , the competitive complexation of HNO_3 to TBP with HTcO_4 reduces the distribution coefficient of ^{99}Tc . In most cases, ^{99}Tc is separated from interferences by TBP extraction in H_2SO_4 solution. It has been reported that the distribution coefficient of ^{99}Tc in H_2SO_4 -TBP medium is a couple of times higher than that in HNO_3 -TBP medium, and about 98% ^{99}Tc can be extracted by TBP in xylene from 2 mol L^{-1} H_2SO_4 [2]. Because of the relatively inert complex behaviour of SO_4^{2-} , ^{99}Tc can be extracted from $1\text{--}6 \text{ mol L}^{-1}$ H_2SO_4 solution by TBP, and the influence of H_2SO_4 concentration is not obvious [5,21]. After the extraction of ^{99}Tc into organic phase, NaOH or $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution is normally used to back-extract ^{99}Tc to aqueous phase for further separation. Although ^{99}Tc can be extracted from H_2SO_4 solution by TBP with a high chemical recovery (usually above 90%), decontamination of Ru in this process is not satisfactory.

Because of the effective separation of Ru and other radionuclides from ^{99}Tc , cyclohexanone has also been used for purification of ^{99}Tc , especially before its measurement by ICP-MS. It has been reported that Ru can be more efficiently removed from ^{99}Tc by extraction using cyclohexanone in K_2CO_3 solution than in HNO_3 medium, although the chemical yield (about 80%) of ^{99}Tc is slightly lower than that in the HNO_3 medium [81]. The adjustment of oxidation states of Ru and Tc in sample solution before extraction is a critical factor which influences the decontamination of Ru. A decontamination factor of 7.0×10^4 for Ru has been reported when sample solution is pre-treated by 30% H_2O_2 in 1 mol L^{-1} K_2CO_3 medium before extraction. In this condition, H_2O_2 acts as a reductant in alkali medium to reduce Ru to low oxidation state, while Tc remains in the form of TcO_4^- . The reduced Ru could not be extracted by cyclohexanone, and remains in the aqueous phase, thus separated from ^{99}Tc which is extracted to the organic phase. It should be mentioned that the decontamination of Mo using

cyclohexanone extraction is not satisfactory [51,102,103], while ^{99}Mo as $^{98}\text{Mo}^1\text{H}$, is one of the major isobaric interferences for ^{99}Tc measurement by mass spectrometry. Therefore, other methods are still needed before measurement of ^{99}Tc .

Solvent extraction offers a great advantage of selection among numerous extractants, whereby the selectivity can be readily modulated. However, there are some disadvantages when the solvent extraction method is used. Firstly, solvent extraction is relative labour-consuming for routine analysis because several extractions should be consecutively performed to separate the analyte from the bulk solution completely. Secondly, a large volume of hazardous organic solvent has to be used, which is harmful not only to the operators, but also to the environment. In recent years, with the development of new chromatography techniques, especially extraction chromatography, solvent extraction is no longer a frequently used technique in routine analysis of environmental samples for ^{99}Tc , and is gradually replaced by anion exchange chromatography and extraction chromatography in many laboratories, although it is still applied in some cases, for example in analysis of high level nuclear waste samples.

2.3.3. Anion exchange chromatography

Anion exchange chromatography is one of the most frequently used separation techniques for determination of ^{99}Tc in environmental samples [17,81,102,104]. Strong basic anion exchange resin, for example Dowex 1 (or Bio-Rad AG1) resin, has a very high selectivity for TcO_4^- anion in a wide range of pH [83,98], because the affinity of TcO_4^- to the resin is much higher compared with other common anions in environmental samples, such as Cl^- , NO_3^- , Br^- , and CO_3^{2-} . Before separation, Tc needs to be converted to TcO_4^- . Addition of H_2O_2 and/or $\text{Na}_2\text{S}_2\text{O}_8$ to the sample solution in acidic medium, normally HNO_3 , is a common method for this purpose. The solution in diluted acid or neutral medium is loaded to an anion exchange chromatographic column, and TcO_4^- , as well as some other anions, are absorbed on the column. Almost all cations and matrix components can be removed in this step. The column is then washed with water, diluted acid including HNO_3 , and HCl to remove the remained cations and most of anions. In earlier works, ^{99}Tc on the column was eluted by NaClO_4 and Na_2SO_3 solution. This exploits the relative higher affinity of ClO_4^- comparing with that of TcO_4^- , and reduction of TcO_4^- to low oxidation state of Tc to enable removal from the anion exchange column [104]. In recent years, high concentration of HNO_3 ($10\text{--}12\text{ mol L}^{-1}$) is often used to elute TcO_4^- from the column. This simplifies the operation of further separation of Tc. However, a low degree of decontamination of Mo and Ru is observed in the eluate, which interferes with the mass spectrometric measurement of ^{99}Tc . Meanwhile radioisotopes of Ru, such as ^{106}Ru and ^{103}Ru , which occurred in the fresh fallout of the nuclear accident and nuclear waste from nuclear power plants, also interfere with the radiometric measurement of ^{99}Tc [81]. It has been reported that Mo absorbed on the column as MoO_4^{2-} can be removed by washing with 0.5 mol L^{-1} HCl , cold and hot water [102], but the decontamination of Ru is still not satisfactory. In order to remove ^{106}Ru in environmental samples contaminated by Chernobyl accident fallout, Chen et al. [61] employed a washing procedure using NaClO solution followed by H_2O_2 and NaOH solution, and reported a better decontamination of ^{106}Ru in the final solution.

Other types of anion exchange resins have also been employed for ^{99}Tc separation [17,42], including macro-pore anion exchange resin (Bio-Rad AG MP-1) and IRA-400. It has been reported that AG MP-1 resin is a useful resin to remove transition elements [17] and Amberlite IRA-400 anion exchange resin is effective to remove Mo [42]. A major advantage of the anion exchange method for separation of Tc is that treatment of large samples is possible, for example up to 200L of seawater, due to the high affinity of

TcO_4^- on the resin. Also, the removal of the matrix components and most interference is effective. Although anion exchange chromatography has been widely used in most analytical procedures for ^{99}Tc , the decontamination factors of some important interfering anions such as RuO_4^- and MoO_4^{2-} are normally not sufficient. The method is therefore not satisfactory for the measurement of low level ^{99}Tc . To obtain a lower detection limit and more accurate analytical results, further separation of Mo, Ru and ^{99}Tc in the eluate of anion exchange chromatography is therefore carried out [20].

2.3.4. Extraction chromatography

Extraction chromatography has advantages of both solvent extraction and chromatography, i.e. combining the selectivity of solvent extraction with the high separation efficiency of the chromatographic method. In this method, the extractant is immobilized on the surface of inert resin beads, corresponding to the organic, stationary phase in solvent extraction and chromatography, respectively. Since commercialization of extraction chromatographic resins by Eichrom Technologies Inc. in 1990s, extraction chromatography has been widely used in radiochemical analysis of ^{99}Tc [7,10,11,21,25,62,73,105–107].

The most commonly used extraction chromatographic resin for ^{99}Tc separation is TEVA® (TEVA), which is produced and commercialized by Eichrom Technologies Inc. The function group on TEVA resin is trialkyl methyl ammonium salt, also called Aliquat® 336. This is mainly used to separate tetravalent actinides and Tc. The separation of Tc using TEVA resin is based on the high affinity of TcO_4^- to TEVA resin in low concentration of acid (K' values are 6×10^3 for 0.1 mol L^{-1} HNO_3 and 6×10^4 in 0.1 mol L^{-1} HCl medium), and the affinity (K' value) decreases with the increase of acid concentration to less than 2 at 8 mol L^{-1} HNO_3 . Therefore it is very useful for the separation of ^{99}Tc from matrix components, and interferences including actinides. Another advantage of TEVA resin is its applicability in the separation of Tc from Ru and Mo, this is based on the great difference in the affinity of TcO_4^- to TEVA compared with those of MoO_4^{2-} and RuO_4^- . Uchida et al. [10] have reported a decontamination factor of 100 for Ru when loading the sample solution in an alkaline solution, compared with a decontamination factor of 250 when loading in 0.1 mol L^{-1} HNO_3 solution. Washing the column with relatively high concentration of HNO_3 increases the removal of Ru from ^{99}Tc . However, it has been observed that a washing solution of HNO_3 with a concentration higher than 4 mol L^{-1} can also remove Tc from the column, resulting in a low chemical yield [108]. The affinity of Tc on TEVA resin decreases with increasing HNO_3 concentration and therefore a high concentration of HNO_3 is used to elute Tc from the resin [25]. Considering the measurement by ICP-MS (normally injecting sample in $0.3\text{--}0.6\text{ mol L}^{-1}$ HNO_3 solution), high concentration of HNO_3 (such as concentrated HNO_3) as eluent requires a high dilution before ICP-MS measurement, resulting in a higher detection limit. Therefore, the eluate of $8\text{--}12\text{ mol L}^{-1}$ of HNO_3 is first evaporated to a small volume and then diluted with deionized water to a HNO_3 concentration of 0.5 mol L^{-1} to improve the detection limit [108].

A common procedure for separation of ^{99}Tc using extraction chromatography with TEVA resin [21,92,103,108,109] is shown in Fig. 5. ^{99}Tc in the sample solution is first converted to TcO_4^- , and the prepared solution in low concentration of HNO_3 (usually 0.1 mol L^{-1} HNO_3 or HCl) is then loaded to a chromatographic column filled with TEVA (about 2 mL) resin. TcO_4^- is absorbed very strongly on the column, while matrix components and most Ru and Mo pass through the column and are separated from ^{99}Tc . The column is washed with $1\text{--}2\text{ mol L}^{-1}$ nitric acid solution to remove the remaining Ru and Mo, as well as other interferences. The TcO_4^- on the column is finally eluted using high concentration nitric acid (usually 8 mol L^{-1} HNO_3).

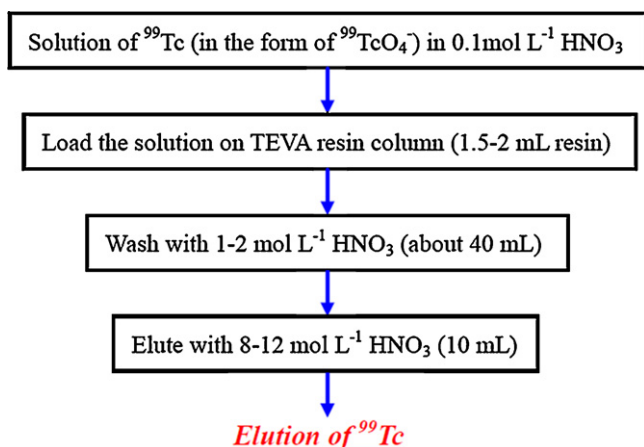


Fig. 5. General procedure for separation of ^{99}Tc by extraction chromatography using TEVA resin.

Besides TEVA, some other types of extraction chromatographic resins such as AnaLig[®] Tc-02 gel, and C_{18} Silica have also been investigated and applied for separation of ^{99}Tc from sample matrices [109,110]. Warwick et al. [110] used C_{18} Silica to purify ^{99}Tc from sample solution. ^{99}Tc was firstly converted to Tc-tripentylamine complex form and prepared in $2 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ medium, and then loaded to a C_{18} Silica column. The column was washed with sulfuric acid/tripentylamine mixture to remove contaminating radionuclides such as Ru, and ^{99}Tc was finally eluted from the column using a dilute alkali solution. Remence [109] has investigated AnaLig[®] Tc-02 gel resin for separation of ^{99}Tc from other radionuclides. The pretreated sample solution was loaded onto the column, and the column was washed with $0.01 \text{ mol L}^{-1} \text{ HCl} + 0.1 \text{ g mL}^{-1} \text{ NaCl}$. ^{99}Tc on the column was then eluted with 10 mL of hot deionized water at $80\text{--}90^\circ\text{C}$. The main advantage of this method is that deionized water is used to elute ^{99}Tc from the column, whereby additional evaporation or dilution steps are avoided before measurement, compared with the TEVA resin, for which high concentration of HNO_3 was used in the elution step. The decontamination of other β emitters is also effective. The decontamination factor for ^{137}Cs is more than 10^5 , and for ^{60}Co about 10^4 . However, comparing with TEVA, these two types of extraction chromatographic resins are less commonly investigated and used, and no decontamination factors for Mo and Ru have been reported using these two types of resins.

The advantages of extraction chromatography, especially employing TEVA resin, are apparent, such as small size column, high decontamination for Mo and Ru interferences, high chemical yield, and less toxic waste production. However, extraction chromatography using TEVA resin is more expensive compared with anion exchange and solvent extraction, which to some extent limits its application for routine analysis.

2.3.5. Combination of different chemical separation and purification techniques

Since the above discussed separation methods have their specific disadvantages in the separation of ^{99}Tc with respect to removal of matrix components and interferences, a single separation method usually cannot result in satisfactory removal of interferences for the determination of low level ^{99}Tc in environmental samples. In addition, the separation efficiency of a specific method also depends on the composition of the sample solution. Poor removal of interferences and low chemical yield might result from the separation if the salt content is very high in the sample solution. In most cases, two or more techniques are combined to improve the decontamination with respect to potential interferences for ^{99}Tc determination. In general, the major matrix

components including alkali and alkaline earth metals, and major anion such Cl^- , Br^- , NO_3^- and SO_4^{2-} , are first removed from the sample by co-precipitation of Tc as Tc(IV) with $\text{Fe}(\text{OH})_2$, and ^{99}Tc is then further purified by extraction chromatography, anion exchange chromatography and/or solvent extraction to remove the interferences, especially Ru and Mo. Chen et al. [6] described an analytical method to determine ^{99}Tc in large volumes of seawater by β counting. ^{99}Tc in the seawater is first pre-concentrated by anion exchange chromatography using Bio-Rad AG 1- \times 4 resin. ^{99}Tc is strongly absorbed on the resin, while most matrix components are removed during the sample loading and washing with diluted HNO_3 . After eluting ^{99}Tc from the column, an AgCl precipitation step is added to remove $^{110\text{m}}\text{Ag}$ which might occur in fresh fallout of nuclear accidents and nuclear power plant releases, and $\text{Fe}(\text{OH})_3$ precipitation follows to remove transition metals. To remove ^{103}Ru and ^{106}Ru , a solvent extraction using 5% TIOA-xylene is followed, combined with evaporation at H_2SO_4 medium. ^{99}Tc in the separated solution is finally purified again by anion exchange chromatography, and a total recovery of about 70% was recorded for 200 L seawater. This method has been successfully applied for routine analysis of seawater samples collected from different locations, and accurate and reliable results were obtained in many intercomparison exercises. However, as mentioned before, the colloids and suspending materials formed during the sample storage may cause a problem during the pre-concentration step using anion exchange chromatography. It should be noted that the procedure is relatively long and time consuming. Keith-Roach et al. [20] have modified this procedure for determination of ^{99}Tc in seawater samples, employing ICP-MS for ^{99}Tc measurement. Fig. 6 shows the schematic diagram of this procedure. The water sample is first acidified to pH less 1.5 with concentrated HNO_3 and then heated at a temperature exceeding 90°C for 2 h to break down any organic complexes and precipitate phases. A hydroxide precipitation step is then added to remove transition metals and actinides, which easily form precipitate in alkali medium. The supernatant is neutralized and loaded to an anion exchange column (AG1- \times 4). Most of the cations are removed to the effluent, after washing the column with water and diluted HNO_3 , and ^{99}Tc is then eluted with $10 \text{ mol L}^{-1} \text{ HNO}_3$ in a small volume. For further separation of Mo and Ru, extraction chromatography using TEVA resin is employed. This procedure overcomes the drawback of pre-concentration of stored water samples using anion exchange AG1-X4 column and also shortens the measurement time by using ICP-MS. However, the complicated pre-treatment and separation procedures prolong the analytical time and decrease the chemical yield of ^{99}Tc in some cases. For determination of ^{99}Tc in solid samples, such as soil, sediment and seaweed samples, ^{99}Tc is normally first separated from the leachate/fusion extracts by co-precipitation or anion exchange chromatography to remove most matrix components. Then a further purification to remove Ru and Mo is carried out before measurement, using solvent extraction or extraction chromatography like TEVA resin. Butterworth et al. [62] have described a method to determine ^{99}Tc in soil and sediment samples using ICP-MS. After destroying organic matter with 30% H_2O_2 , concentrated HCl was used to leach ^{99}Tc from the sample matrix. The transition metals, actinides and lanthanides were first removed by precipitation using $\text{Fe}(\text{OH})_3$, and alkali as well as alkaline earth metals remaining in the solution with ^{99}Tc were then removed using anion exchange chromatography (Dowex 1- \times 8). An evaporation step was followed to reduce the size of the eluate. The obtained solution was then diluted to $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ for further decontamination of Ru and Mo by extraction chromatography with TEVA resin. Most matrix components and interferences can be removed in this procedure and a relatively clean solution was obtained prior to the measurement by ICP-MS. The main drawbacks of the method appear to be the time consumption during the

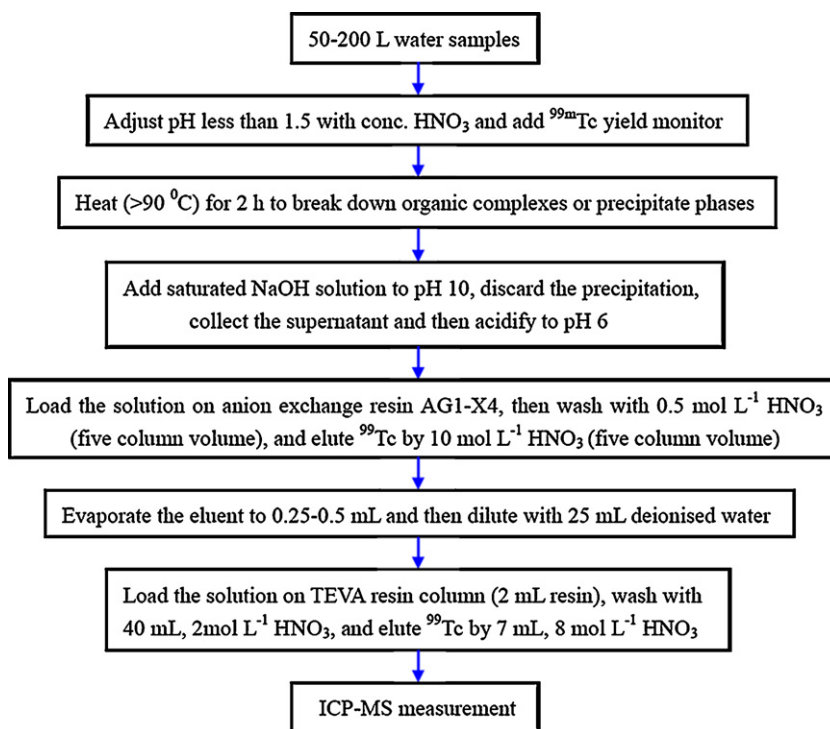


Fig. 6. An analytical procedure for the determination of ^{99}Tc in large volume water sample [20].

evaporation step and the relatively inefficient decontamination of Mo and Ru since washing with $0.5 \text{ mol L}^{-1} \text{HNO}_3$ in the TEVA purification step is not enough to remove all of Mo and Ru. McCartney et al. [11] have proposed a simple method to remove the matrix components in the leachate by re-crystallisation. The leachate from a solid sample was evaporated to incipient dryness. The residue was then leached with a small volume of water (30 mL for 10 samples), and the leachate was used for further separation of ^{99}Tc . It has been reported that chemical yield of ^{99}Tc in this step is higher than 98%, while most matrix elements including the salts of alkali and alkaline earth metals, transition metals, and actinides are removed. It was also observed that about 20% of Ru can be removed in this step. Although this method can remove most matrix elements and is simple to operate, the efficiency of matrix removal is normally mild, which may reduce the separation efficiency in the further purification steps. However, if large samples are analysed, loss of ^{99}Tc in the re-crystallisation step might become significant, which will result in a low chemical yield of ^{99}Tc in the whole procedure. In general, most reported analytical procedures for ^{99}Tc determination in environmental samples are tedious and time consuming. The development of a high efficiency method with a short analytical time, while providing high decontamination of interferences and low detection limits, as well as reducing the cost of the analysis is still a challenge in the determination of ^{99}Tc in environmental samples.

2.4. Source preparation for measurement of technetium-99

As a pure β^- emitter, ^{99}Tc is conventionally measured by radiometric methods including LSC [7,8,69] and GM-gas flow counter [61,78,111]. In recent years, more and more measurements of ^{99}Tc are carried out by mass spectrometry, especially ICP-MS. Depending on the measurement techniques, the separated ^{99}Tc has to be prepared in a suitable medium before measurement. For the detection of ^{99}Tc by LSC, the ^{99}Tc solution separated from matrix and

interfering radionuclides and in a small volume (<5 mL) has to be mixed with scintillation cocktail for activity measurement. If the ^{99}Tc is in an organic solution, which is fully soluble in the scintillation cocktail, and therefore a high compatible with scintillation cocktail and consequentially a high counting efficiency. Most frequently, ^{99}Tc is in an aqueous solution which is not completely compatible in the organic cocktail. Especially for a solution with high salt content, high acid or alkali concentration, a high quench (low counting efficiency) will occur, and it is normally necessary to prepare the solution in diluted acid/alkali solution with less salt content to be able to obtain a high counting efficiency, and therefore a low detection limit. For measurement with GM-gas flow counter, the sample is normally prepared in solid form and the amount of the final sample should be as small as possible to minimize self-absorption. Co-precipitation and electrodeposition are frequently used methods for preparing counting sources for measurement using GM counter. Co-precipitation methods, e.g., reducing TcO_4^- to low oxidation state and co-precipitating with $\text{Fe}(\text{OH})_2$ or CuS , has been used. However, because of the low recovery and reproducibility, as well as the relatively large mass of precipitation which increases self adsorption, this technique is not a commonly used method for solid source preparation. Electro-deposition is the most commonly used source preparation method for measurement of ^{99}Tc by GM counter [61,78,111]. Electro-deposition of ^{99}Tc onto a metal disk (normally a stainless steel disk) can be carried out in various media, including oxalic acid, sulfuric acid, and NaOH solution [45,61]. It has been reported that a yield of 98% for ^{99}Tc could be obtained when the electro-deposition was carried out in oxalic acid and sulfuric acid medium on a bronze disc under the current of 200 mA for 8 h. A shorter electro-deposition time of only 4 h has also been used for ^{99}Tc on stainless steel disks in $1\text{--}2 \text{ mol L}^{-1} \text{NaOH}$ solution, which produced a yield of 95–100% under a direct current of 300 mA. The disk with electrodeposited ^{99}Tc needs to be quickly rinsed with water at pH 9 to remove any salt on the disk surface, and then dried at $80\text{--}90^\circ\text{C}$ before measurement [61].

In the case of mass spectrometric measurement, the final source of ^{99}Tc has to be prepared in a form that depends on the mass spectrometric technique to be employed. For instance for measurement using RIMS, the separated ^{99}Tc is electroplated or evaporated onto Re filaments [112]. The source for AMS is normally prepared as oxides, and is pressed in a target holder. A high pure aluminum power with a known concentration of Re solution or niobium is added to the eluate of ^{99}Tc in HNO_3 solution, which is then evaporated to dryness, and the residue is baked at 400–450 °C under nitrogen gas flow for 1 h to form Tc and carrier metal oxides [15,16]. If samples are measured by ICP-MS, especially when a sample introduction system of solution is applied, the final solution is normally prepared in diluted HNO_3 medium, e.g. 0.3–0.6 mol L $^{-1}$ HNO_3 , and low salt content is normally needed to obtain a high measurement efficiency [98]. When an electrothermal vaporization (ETV) system is applied for introducing sample to the system for ICP-MS measurement, the final sample in a very small volume of solution, normally a few tens of microlitres, is transferred to an electrically conductive cell for analysis. It has been reported that the addition of NaClO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$ to the solution as chemical modifier can improve the signal intensity of ^{99}Tc in the ICP-MS measurement [19,113]. In this case, the ^{99}Tc in 8–10 mol L $^{-1}$ HNO_3 eluate from extraction chromatography or anion exchange chromatography is evaporated to near dryness. After re-dissolving in 0.1 mol L $^{-1}$ HNO_3 , a small amount of NaClO_3 or $\text{NH}_3\cdot\text{H}_2\text{O}$ is added to prepare a final solution for ETV-ICP-MS measurement.

2.5. Measurement techniques for technetium-99

Both radiometric and mass spectrometric techniques have been used for measurement of ^{99}Tc , these techniques include β counting using GM gas flow counter and LSC, neutron activation analysis, ICP-MS, TIMS, RIMS and AMS. Of these, the GM gas flow counter and ICP-MS are the most commonly used techniques.

2.5.1. Radiometric methods

As a pure β^- emitter, ^{99}Tc can be detected by β counting using gas ionization detector or LSC. Compared to the MS techniques, these methods have lower cost, relatively higher reliability and easier operation. However, counting time is much longer than with MS techniques, and the detection limit of LSC is normally higher compared with mass spectrometric methods, due to high background level. In addition, the neutron activation analysis (NAA) has also been used for the detection of ^{99}Tc . These techniques are discussed and compared below.

2.5.1.1. β -Counting. LSC has been accepted as the generally preferred method for counting soft β emitters such as ^{99}Tc (a pure β^- emitter with a maximum energy of 0.294 MeV) [8,96]. This technique is based on radiation-induced light formation and transformation of the light into electric pulses. It has the following characteristics: negligible self-absorption, no absorption of radiation by air or in detector window, no radiation scattering prior to incidence upon the detector and 4π counting [22]. The counting efficiency of this method for ^{99}Tc measurement, depending on quench level and the width of the energy windows selected, ranges from 75% to 98%. Compared with other radiometric methods, simple source preparation and short counting time are main advantages of LSC. However, the higher detection limit of the technique constitutes a restriction for its application, especially for low level ^{99}Tc determination. This is attributed to the relatively high background/blank counts of this technique, even for low level background instruments, such as Quantulus. A detection limit of 17 mBq (equal to 2.7×10^{-11} g ^{99}Tc) has been reported with a counting time of 2 h and counting efficiency of 90% [8].

In addition to the high detection limit, quench is another drawback during LSC determination. Color or chemical quench from the undesired chemicals in the final sample solution should be taken into account [68]. Ideally all potential quenching reagents need to be removed from the samples before measurement. Among various quenches, acid and alkali solutions, as well as various salts in the final sample solution are the common quench reagents. However, the sample volume should also be reduced as much as possible to be able to reduce quench and thus improve counting efficiency.

Gas ionization detection, especially by gas flow GM counter, is a traditional technique, which has been widely applied for β emitter (such as ^{99}Tc) detection [5,61]. Gas proportional counters have also been used for measurement of ^{99}Tc in early days (1980s), but seldom used in present days because of their poor detection limit. The counting efficiency of a GM counter varies from 10% to 70% depending on the energy of the emitted β particles, thickness of the source, and counter properties [22]. For low level ^{99}Tc analysis in environmental samples, a low background GM counter is required. This is mainly achieved by using lead shielding and guard detectors above the sample detectors, and operating in anti-coincidence mode with the sample detectors. The detection limit of this technique depends on the count rate of blanks and the counting time. A typical detection limit by gas flow GM detector is of the order of several mBq, which corresponds to about 10^{-12} g of ^{99}Tc [61]. Although there are several advantages of gas flow GM detectors, like the relatively low detection limit, the long counting time is usually the main drawback for its application compared with MS methods.

Because of the advantage of low cost and easy access in most of radiochemical laboratories, the β counting technique has been the most widely used method for measurement of ^{99}Tc in both environmental and waste samples. It normally provides a reliable analytical result because a high separation efficiency of interferences from other radionuclides is easily achieved especially when LSC is used for measurement. However, the detection limits of these methods, especially LSC, are high, and consequently, large samples would be required to reach a suitable detection limit for analysis of low level environmental samples. Also, these techniques are time consuming. Normally several hours to days are needed according to the concentration of ^{99}Tc . Consequently, β counting methods are not suitable for measurement of samples in emergency situations, where analytical results should be obtained within a shorter time frame (less than one day).

2.5.1.2. Neutron activation analysis (NAA). NAA, based on the two reactions $^{99}\text{Tc} (n, \gamma) ^{100}\text{Tc}$ and $^{99}\text{Tc} (n, n') ^{99m}\text{Tc}$, can also be used for measurement of ^{99}Tc [22]. It is theoretically a more sensitive method for ^{99}Tc , and detection limits ranging from 10^{-12} to 10^{-9} g have been obtained, depending on the Tc isotope counted [114]. When counting ^{100}Tc , separation of ^{99}Tc from the sample matrix and purification of ^{99}Tc is necessary because of the very short half-life of ^{100}Tc (β emitter, half-life of 15.8 s). A fast sample transfer system has to be used. Foti et al. [84] developed a fast radiochemical separation procedure based on the precipitation of $\text{Fe}(\text{OH})_3$ to remove metals, co-precipitation of Tc with tetraphenylarsonium perhenate, and evaporation of tetraphenylarsonium perhenate by heating. The whole separation procedure can be completed in 40–45 s. Due to the low γ ray emission probability of ^{100}Tc (7% for 539.5 keV, 5.7% for 590.8 keV γ ray), low background β counters have been used to detect ^{100}Tc (a β emitter with maximum energy of 3.02 MeV), to improve the counting efficiency. In this case, post-irradiation separation has to be completed to get a high purity ^{100}Tc source and a lower detection limit of 5×10^{-11} g has been obtained by this method.

Compared with ^{100}Tc , $^{99\text{m}}\text{Tc}$ has a relatively long half-life, which makes the post-irradiation separation easier. However, the low neutron activation cross section (0.24 b) of the ^{99}Tc (n, n') $^{99\text{m}}\text{Tc}$ reaction limits its analytical sensitivity [115]. The reported detection limit of this method is more than 10^{-9} g, which is even higher than that of LSC and is insufficient for the measurement of ^{99}Tc in environmental samples [116]. So far, NAA has mainly been used for analysis of samples with high ^{99}Tc concentration, such as radioactive waste. The application of this method for analysis of ^{99}Tc in environmental samples is still limited because of the relatively short half-life of ^{100}Tc , and because a nuclear reactor is required.

2.5.2. Mass spectrometric methods

With the advantages of high sensitivity and short analysis time, MS has been applied in many areas and studied extensively, also in recent years for measurement of ^{99}Tc , especially in low level environmental samples [14–21,112,117–119]. The first trace-level analysis of ^{99}Tc using MS was reported by Anderson et al. in 1980 [87]. Since then, extensive measurement of ^{99}Tc has been carried out using this technique. So far, several MS techniques, including AMS [14–16], RIMS [112,117], TIMS [17,118,119], and the popular ICP-MS [18–21], have been introduced to determine the concentration of ^{99}Tc .

2.5.2.1. Inductively coupled plasma-mass spectrometry (ICP-MS)

ICP-MS is a relatively powerful technique which has been extensively utilized to determine ^{99}Tc in environmental samples [18–21,75,88,120–122]. Compared with β -counting, ICP-MS possesses evident advantages including short analytical time (usually several minutes per sample) and relatively high sensitivity. The first measurement of ^{99}Tc using ICP-MS in environmental samples was reported in 1989 by Kim et al. [18]. In their work, sample solution was introduced to ICP-MS by a common concentric nebulizer. A detection limit of 10^{-12} g (about 1 mBq) was reported, which is lower than that achievable with LSC and comparable to that of GM counters. Since then, application of ICP-MS for measurement of ^{99}Tc has rapidly increased, mean while this analytical technique has been optimized and improved. By applying a Meinhard Type C nebulizer for sample introduction into a Scotts water-cooled spray chamber, Beal et al. [25] improved the detection limit to pg mL^{-1} level. Due to the very low introduction efficiency of the conventional concentric/cross flow nebulizer (<1%), many efforts have been made to improve the analytical sensitivity of ICP-MS, employing high efficiency nebulizers, such as ultrasonic nebulizers (USN), microconcentric nebulizers (MCN), direct injection high efficiency nebulizers (DIHEN), and electrothermal vaporization devices (ETV). It has been reported that the detection limit of quadrupole ICP-MS for ^{99}Tc has been improved more than 10 times to 3×10^{-14} g mL^{-1} using an ultrasonic nebulizer instead of the conventional concentric nebulizer [42].

Using an ETV system for sample introduction, Hepiegne et al. [123] reported a detection limit of 2×10^{-13} g mL^{-1} for ^{99}Tc measured by quadrupole ICP-MS. This is attributed to the high introduction efficiency of ETV (70–100%) comparing with concentric nebulizers. To improve the removal of Ru, Song et al. [19] described a method where NaClO_3 (0.7%) and HNO_3 (1%) was added as modifiers to the samples. Selecting a suitable evaporation temperature, the Ru signal can then be significantly suppressed, thus providing an extra decontamination of Ru in the ICP-MS measurement. At the same time, the detection limit and analytical reliability of the ^{99}Tc measurements are also significantly improved. Recently, Skipperud et al. [113] reported a similar method: by employing $\text{NH}_3 \cdot \text{H}_2\text{O}$ as the modifier, they observed a similar suppression of the Ru signal as that obtained using NaClO_3 and HNO_3 , but a more stable ^{99}Tc signal during measurement. A detection limit of

5×10^{-13} g mL^{-1} of ^{99}Tc has been recorded using this method with quadrupole ICP-MS. However, it should be mentioned that as ETV-ICP-MS requires small sample volume (a few microliter), the final ^{99}Tc solution eluted from the chromatographic column has to be concentrated to a few microlitres by evaporation, which increases the time required for sample preparation.

Compared with quadrupole type ICP-MS, high resolution ICP-MS (HR-ICP-MS) is more sensitive and enables removal of some polymolecular ions interference [124]. A detection limit of 10^{-13} g ^{99}Tc has been obtained using HR-ICP-MS, which is about 10 times lower than that obtained by β counting and quadrupole type ICP-MS with the same concentric sample introduction system, and comparable with that of quadrupole ICP-MS with ETV sample introduction [20,102]. Although HR-ICP-MS has high sensitivity for ^{99}Tc , a limiting factor is the high cost of the instrument.

To normalize any drift and instability of the instrument response, an internal standard needs to be added to the sample before measurement. In general, the internal standard should have a similar ionization potential and a mass in the same region as the analyte [97]. ^{103}Rh fulfils most of these demands but it is difficult to stabilize in weak HNO_3 solutions for prolonged periods. McCartney et al. [11] tested different nuclides as internal standard and reported that the behaviour of ^{115}In is most similar to that of ^{99}Tc , and the potential risk of disturbing the mass 115 by $^{99}\text{Tc}^{16}\text{O}$ is insignificant. The memory effects of In are easily eliminated compared with Rh. In practice, ^{115}In is most frequently used as an internal standard not only for ^{99}Tc measurement, but also for many other isotopes. It should be mentioned that when using long-lived Tc isotopes (^{97}Tc and ^{98}Tc , as well as stable ^{185}Re and ^{187}Re), as yield tracer, no extra internal standard is needed, because these yield tracers can also act as internal standard for the normalization of the instrument for ^{99}Tc measurement.

ICP-MS is a rapid, sensitive and suitable method for determination of low level ^{99}Tc . The major challenge of this analytical technique is the isobaric and spectrometric interferences, which will not only raise the detection limit of the method, but also reduce the reliability of the analytical results. Also, high concentrations of matrix elements may lead to signal suppression [75], and consequently, reduced sensitivity. The concentration of total dissolved solid in the sample solution generally needs to be kept below 0.1%. Effective separation and purification, especially for Ru and Mo, is particularly critical for accurate determination of ^{99}Tc in low level samples. Several separation procedures are often combined, especially for samples with high concentration of Mo and Ru, which in some case increase the analytical time. Clean laboratory conditions, including glassware, as well as high quality chemicals are also required to avoid contamination of Ru, Mo and other interferences during the sample preparation.

2.5.2.2. Accelerator mass spectrometry (AMS)

AMS is the most sensitive method for determination of low level radionuclides in environmental samples, and has been applied for measurement of ^{99}Tc . The major advantage of this method is its high sensitivity. Consequently, small amounts of sample are required [125]. The challenge in connection with AMS measurement of ^{99}Tc is related to the isobaric interference of ^{99}Ru [126].

In AMS measurement, negative ions of Tc or its compound are generated in a Cs sputter source, and pass through a magnetic sector where they are accelerated through a potential of several MV to a positive terminal. At the terminal, a passage through a thin foil or low pressure gas generates positive ions of high charge, which then accelerate back to ground potential where they pass through further electrostatic and magnetic selection, and are finally measured by ion detector (normally ionization chamber). AMS is a relative analytical method, i.e. it gives a ratio of two isotopes, normally

the target isotope and another isotope of the same element (e.g., $^{129}\text{I}/^{127}\text{I}$ for ^{129}I measurement and $^{239}\text{Pu}/^{242}\text{Pu}$ for ^{239}Pu measurement; Here ^{127}I is the stable isotope of iodine and ^{242}Pu is another radioactive isotope of plutonium). Because there is no stable isotope of Tc in nature, long-lived isotopes of Tc, e.g. ^{97}Tc and ^{98}Tc , are used for this purpose. However, Mo typically exists as impurity and/or contamination in the Cs ion source in the AMS. ^{97}Mo and ^{98}Mo are stable isotopes with similar mass as ^{97}Tc and ^{98}Tc and can give a very high background, which prohibits the application of ^{97}Tc and ^{98}Tc in AMS measurement of ^{99}Tc . Therefore an isotope of an other element has to be used for the AMS measurement. ^{185}Re , ^{187}Re and ^{93}Nb are the most widely used isotopes for normalization of ^{99}Tc signal in AMS measurement. In this case, ^{185}Re , ^{187}Re or ^{93}Nb is measured by Faraday cup, while ^{99}Tc is measured by ionization chamber, and a ratio of $^{99}\text{Tc}/^{185}\text{Re}$, $^{99}\text{Tc}/^{187}\text{Re}$ or $^{99}\text{Tc}/^{93}\text{Nb}$ is presented. Based on the amount of carrier (Re or Nb) added to the separated Tc solution during source preparation, the ^{99}Tc content in the separated final sample can be calculated, and taking into account the chemical yield measured by tracer, the ^{99}Tc concentration in the sample can be estimated.

The very small difference in the atomic mass of ^{99}Ru and ^{99}Tc ($\Delta m = 0.0003154\text{ u}$) makes the isolation of ^{99}Ru from ^{99}Tc in AMS difficult, and therefore ^{99}Ru is the major interference in the AMS measurement of ^{99}Tc . Removal of ^{99}Ru from ^{99}Tc by chemical separation is needed before the AMS measurement of ^{99}Tc . Extraction chromatography using TEVA resin for measurement of ^{99}Tc by ICP-MS can also be used for determination of ^{99}Tc using AMS. Discrimination between ^{99}Tc and ^{99}Ru using physical methods in AMS has been investigated intensively. A small difference in the energy loss of ^{99}Tc and ^{99}Ru ions in the gas ionization chamber has been used to discriminate ^{99}Ru from ^{99}Tc , using multiple anodes for measurement of the energy loss of the ions as they slow down in the gas ionization chamber. This is only effective when the ion energy is at least 120 MeV [16]. Hence a large accelerator operating at more than 10 MV is required for this purpose. It has been reported that up to 90% of the ^{99}Ru can be discriminated from ^{99}Tc when an 8 segmented anode is used for measurement of energy loss in the ionization chamber, and Tc ions are accelerated to 220 MeV Tc^{14+} using a 14.5 MV accelerator [14]. Fifield et al. [15] reported another method to eliminate the interference of ^{99}Ru by quantifying and subtracting the contribution of ^{99}Ru from ^{99}Tc by accounting for ^{101}Ru and using the natural ratio of $^{99}\text{Ru}/^{101}\text{Ru}$. The detection limit of AMS for ^{99}Tc could be as high as 10^{-15} g using this method. However, a large uncertainty results if the energy loss information from the detector is used to reject the bulk of the ^{99}Ru .

Negative ions of both $^{99}\text{Tc}^-$ and $^{99}\text{TcO}^-$ can be formed in the ion source with similar prolificacy [14,15], but the yield of Ru^- is much higher than that of the RuO^- ion (the Ru^-/RuO^- yield ratio is about 6). The ^{99}Ru signal can be suppressed to some extent using oxide ions [15], and therefore the negative oxide ion $^{99}\text{TcO}^-$ is often applied as the analyte for ^{99}Tc measurement by AMS. It has been reported that the yield of TcC^- is much higher than that of TcO^- (with a ratio of $\text{TcC}^-/\text{TcO}^-$ of 25), whereas similar yields of RuC^- and RuO^- have been measured (with a ratio of $\text{RuC}^-/\text{RuO}^-$ of only 1.3). This provides a potential for better suppression of Ru in AMS measurement of ^{99}Tc [127]. In this case, the source of Tc should be prepared by mixing Tc oxide with graphite. A new investigation has shown a preferable formation of TcF_4^- compared with RuF_4^- . Therefore orders of magnitude suppression of the Ru signal is expected when using this method without employing a high energy accelerator [128].

Although AMS can provide a better detection limit for ^{99}Tc measurement, the high cost and less availability of AMS limits the use of this technique as a routine measurement method for ^{99}Tc . With the increased numbers of AMS facilities installed in the recent years, the application of this technique for ^{99}Tc measurement will become

more popular and much lower level of ^{99}Tc can be detected with small sample size.

2.5.2.3. Other mass spectrometric methods. In addition to ICP-MS and AMS, some other MS methods have also been used to measure ^{99}Tc in environmental samples. Thermal ionization mass spectrometry (TIMS) and resonance ionization mass spectrometry (RIMS) are two of the important ones [17,112,117–119]. TIMS with multiple ion collectors is generally the method of choice for isotope ratio measurements with high precision (down to 0.002%). ^{99}Tc levels from 10^{-9} g down to less than 10^{-15} g (6×10^6 atoms) have been successfully measured with ionization efficiencies of more than 2% using negative thermal ionization [118]. However, the interferences from iodine (I^-) and the complex molecule molybdenum fluoride trioxide (MoFO_3^-) are the main problems in analysis of environmental samples using TIMS. The I^- ion might form an ion cloud which greatly reduces TcO_4^- ion production and transmission, causing a count rate drop to nearly zero. The MoFO_3^- ions, mainly formed on the hot thermal surface, can cause two analytical problems: (i) isobaric interference that requires large corrections to the data, and (ii) reduction of ionization efficiency of TcO_4^- . It has been reported that a longer filament heating time at 930°C can efficiently remove I^- , while TcO_4^- still remains on the filament. To eliminate MoFO_3^- interference, Dixon et al. [17] described a method in which small amounts of $\text{Ca}(\text{NO}_3)_2$ (usually $1\text{ }\mu\text{L}$ of 0.0165 mol L^{-1}) were added to the sample, which was dried at 80°C prior to loading onto the filament. It was explained that Ca^{2+} may interact with MoFO_3^- and suppress its volatility. A detection limit of 10^{-14} g has been obtained using this technique for environmental samples. Although the sensitivity of TIMS for ^{99}Tc is better than that of ICP-MS, the size of the sample loaded to the filament for measurement is normally very small (a few microlitres), and the sample preparation is very time consuming and labour intensive. Also, the high cost and poor accessibility of the instrument are reasons why TIMS is not often used for measurement of ^{99}Tc in environmental samples.

RIMS has also been applied for ^{99}Tc measurement in environmental samples. In connection with resonance ionization analyses, two critical aspects need to be considered: selectivity and sensitivity. In terms of selectivity, Mo and Ru are the main interferences which might cause poor analytical results. It has been reported that three-photon ionization of ^{99}Tc shows a good RIMS scheme for analysis of samples containing Mo [117]. Free Mo has not known visible electronic transitions originating from the ground state and the potential for photo-ionizing Mo is also much low. The mass spectral interference of Ru can be reduced using the multiplicative selectivity of multiple resonance as well as proper selection of ionization schemes [129]. The major impediment to realize the ultimate sensitivity of RIMS lies in the amount of the Tc in the samples which is evaporated as atoms. Initial RIMS studies of ^{99}Tc were carried out using a tunable ultraviolet pulse laser via a resonant two-photon ionization scheme [130], but the sensitivity for ^{99}Tc is relatively low. Downey et al. [117] reported on a technique using a three-photon, two-color resonance ionization scheme for mass spectrometric analysis of ^{99}Tc . Samples containing more than 10^8 atoms of ^{99}Tc ($>10^{-14}\text{ g Tc}$) could be detected by RIMS if 100% of the sample evaporates as atoms. However, because of the loss of ^{99}Tc during the sample preparation, like failure to evaporate ^{99}Tc or evaporation in a non-analyzable (molecular) form, the ionization efficiency of ^{99}Tc is always low and high detection limit is obtained. In order to improve the ionization efficiency as well as the sensitivity of RIMS, Trautmann [112] proposed a method using three-color, three-step resonant excitation via an auto-ionizing state with a high-repetitive pulsed laser system for ^{99}Tc detection. Instead of the filament technique, a laser ion source has been used in the

Table 7
Comparison of different techniques for ^{99}Tc detection.

Method	Detection limit	Detection time	Analysis cost	Reference
LSC	10^{-10} – 10^{-11} g	h	Fair/low	[7,8,96]
GM counting	10^{-11} – 10^{-12} g	Days	Fair/low	[5,61]
NAA	10^{-9} – 10^{-12} g	min ~ h	High	[84,114]
ICP-MS	$\sim 10^{-12}$ g	min ~ h	Low	[18,19,21]
TIMS	$\sim 10^{-15}$ g	min ~ h	High	[118,119]
RIMS	$\sim 10^{-15}$ g	min ~ h	Very high	[112,117]
AMS	$\sim 10^{-15}$ g	min ~ h	Very high	[14,15]
ETV-ICP-MS	10^{-13} – 10^{-14} g	min ~ h	Relatively high	[19,113]
HR-ICP-MS	$\sim 10^{-13}$ g	min ~ h	Relatively High	[102]

RIMS schemes. The laser ion source consists of many cavities with a small hole to inject the laser beams and to extract the photoions; the atoms of Tc are confined inside the cavity and can interact several times with the laser light. An overall efficiency of 4×10^{-4} and a detection limit of 10^6 atoms of ^{99}Tc (10^{-16} g ^{99}Tc) have been obtained, which is about two orders of magnitude better than that obtained with the filament technique. Compared with other methods, RIMS has some advantages, such as good overall efficiency, strong suppression of atomic or molecular isobaric interference, high isotopic selectivity and low background. However, there are still no commercial RIMS instruments available, which makes the technique rather rare in application compared with the other MS techniques such as ICP-MS.

2.5.3. Comparison of different measurement techniques

Table 7 summarizes the major detection techniques for ^{99}Tc by comparing their detection limits and analytical cost. β counting is the traditional detection technique, which has been extensively applied for measurement of ^{99}Tc in environmental samples as well as in various waste samples. It is still a powerful and often used technique for routine analysis of environmental samples for ^{99}Tc because of the simplicity of measurement, reliability and reasonable sensitivity. However, long counting time and interference from other radionuclides are the major disadvantages. A relatively quick measurement can be achieved by LSC after a thorough separation of ^{99}Tc from other radionuclides, while the relatively high detection limit is its major demerit. NAA as a radiometric technique can also be used for measurement of ^{99}Tc with a reasonable detection limit if the $^{99}\text{Tc}(n, \gamma)^{100}\text{Tc}$ reaction is employed and ^{100}Tc is counted. However, a fast separation of the short-lived ^{100}Tc formed by neutron activation of ^{99}Tc is needed; in addition a nuclear reactor is also required for this work. This technique is therefore seldom used for determination of ^{99}Tc in environmental samples. ICP-MS has become a commonly used technique for measurement of ^{99}Tc in environmental samples. This is attributed to its rapid analytical capacity, relatively high sensitivity, low cost and high accessibility. The major challenge in ICP-MS measurement for ^{99}Tc is the isobaric interferences at mass 99 contributed from stable isotopes (mainly ^{99}Ru and $^{98}\text{Mo}^1\text{H}$). To obtain a reliable analytical result and sufficiently low detection limit, it is necessary to carry out a thorough decontamination of Ru and Mo, as well as other matrix elements before measurement. Also high quality laboratory conditions, including glassware, air and chemicals are key parameters to ensure sufficiently low reagent blank at mass 99. TIMS and AMS can provide higher sensitivity and even better detection limit, but the analysis is costly and the instruments are not easy to assess. Therefore these methods are not often used for determination of ^{99}Tc in environmental samples. For TIMS, a special separation procedure is needed to obtain a small sample solution and good precision of isotopic measurements. It is always time consuming and labour intensive. AMS operation is more complex and a well experienced team is required, although a very low detection limit can be obtained. Yet, this detection technique is becoming increasingly

popular because of instrumental developments. The application of RIMS is still limited because there are no commercial RIMS instruments available at present.

In summary, although a lot of techniques can be used for measurement of ^{99}Tc , the most frequently used are β counting using GM counter and ICP-MS. The detection limits of these two techniques are similar if quadruple ICP-MS and low background GM counters are used.

3. Automated analytical methods for technetium-99 determination

Due to the low concentration of ^{99}Tc in environmental samples, a thorough chemical separation of matrix components and interferences is required before measurement of ^{99}Tc . As described above, this chemical separation is often time consuming and labour intensive, which increases the analytical cost and limits the analytical capacity. The development of automated analytical methods is an approach to overcome these drawbacks. Automation of the analytical procedure can also reduce the risk of exposure of operators to the hazardous chemicals and thus enhance the safety. With the increased requirement for rapid radiochemical analysis for emergency situations, such as nuclear accidents and radiological attacks, automated and rapid analytical methods become more and more important.

Although some automated analysis procedures have been reported for determination of radionuclides like Pu in environmental samples [131], the application of these approaches for ^{99}Tc determination is still limited and only applied in few laboratories [91,132]. In early studies, the automation of the analysis of ^{99}Tc is mainly focused on the separation step using anion exchange or extraction chromatography techniques. Hollenbach et al. [133] reported a method using a flow injection system for on-line separation of ^{99}Tc in small soil samples. After pretreatment, the sample solution was pumped through a mini-column packed with TEVA (50 μL resin), TcO_4^- was absorbed on the column and separated from the matrix components and interferences. ^{99}Tc on the column was then eluted and measured by ICP-MS through injection of eluate directly into the instrument. For a 0.25 g soil sample, a detection limit of 11 mBq g^{-1} (1.72×10^{-11} g g^{-1}) has been reported. Compared with the conventional manual procedure, separation using flow injection system is faster and less labour intensive; however, because a small column is applied for ^{99}Tc purification, the decontamination of Mo and Ru is poor, especially for large samples, if no other separation method is included, which causes a poor detection limit for ^{99}Tc . Egorov et al. [132] introduced an approach using a FIA Lab 3000 sequential injection system with stopped flow radiometric detection for automated determination of ^{99}Tc in nuclear waste. Fig. 7 shows the schematic diagram of this system. The on-line separation is carried out using a TEVA column (20–50 μm , 0.83 mL). The eluate of ^{99}Tc from the column is directly measured using a flow radiometric detector. All operation in a closed system is carried out in a fully automated model by computer control, and

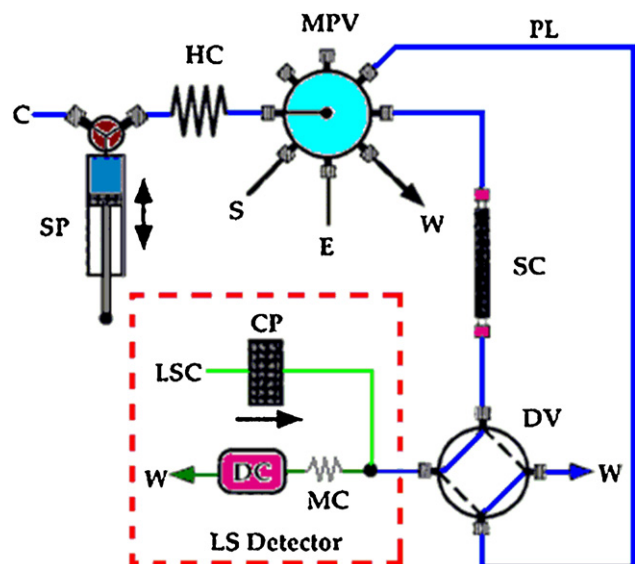


Fig. 7. A schematic diagram of the sequential injection ^{99}Tc analyzer (Adapted from Ref. [132] with permission from American Chemical Society). C: carrier (water); SP: Syringe pump; HC: holding coil; S: sample line; E: eluent line; W: waste; MPV: multiposition valve; SC: TEVA resin column; PL: purge line; DV: two-way diverter valve; LSC: liquid scintillation cocktail; CP: cocktail pump; DC: detector flow cell; MC: mixing coil.

one analysis can be completed in 20–40 min, excluding the sample pre-treatment. Nuclear waste samples (e.g. 1 mL) from storage tanks of a reprocessing plant have been successfully analysed using this method. Compared with the continuous flow injection with peristaltic pump, the sequential injection system is more flexible and attractive. For example, the syringe pump can eliminate the frequent pump tubing replacement and tedious flow rate calibrations. However, as mentioned above, the method can only be applied for analysis of small samples, and is not suitable for analysis of environmental samples with low level of ^{99}Tc .

Kim et al. [91] have described a different automated separation system for determination of low level ^{99}Tc in soil samples using an on-line flow injection system. Two TEVA columns with different sizes (0.75 and 0.17 mL) were employed to remove the interferences. The whole separation could be finished in 53 min for one analysis. Because of the application of two chromatographic columns, the removal of interferences is effective, and decontamination factors of 1.6×10^4 for Mo and 9.9×10^5 for Ru have been reported, and therefore a relatively low detection limit of 0.05 mBq mL^{-1} ($7.8 \times 10^{-14} \text{ g mL}^{-1}$) for ^{99}Tc was obtained by HR-ICP-MS measurement. However, as most other on-line analytical methods, the samples are processed one after another during the separation process, which might increase the analytical time. In addition, the sample size is still restricted to a few grams in this system, and not suitable for analysis of environmental samples with very low level of ^{99}Tc .

For low level environmental samples, the pre-treatment process is usually carried out manually. However, for nuclear waste, especially high level nuclear waste, fully automated analysis is necessary to reduce the risk of the exposure of the operator to the radioactive materials. Egorov et al. [134] have described an analytical approach for determination of ^{99}Tc in aged nuclear waste streams. A fluid handling step, including acidification of caustic sample and microwave-assisted sample digestion using peroxodisulfate oxidant were applied for sample pre-treatment. The prepared sample was then directed to an anion exchange chromatography equipment using AG MP-1 resin (0.83 mL) for separation of ^{99}Tc . The eluate was directly delivered to a flow-through

scintillation detector for measurement. This procedure has been applied successfully for determination of ^{99}Tc in aged nuclear waste samples, but the feasibility for separation and analysis of ^{99}Tc from fresh nuclear waste samples with more interfering radionuclides, as well as from other large environmental samples might be not satisfactory. Automated sample pre-treatment is a difficult step in the automation of analytical procedures for ^{99}Tc in different types of samples. Therefore an on-line multi-sample analytical system as well as a fully automated analysis procedure will be the two major future challenges for automated analysis of ^{99}Tc in environmental samples.

4. Conclusions and perspectives

Important aspects governing the reliability of measurements of ^{99}Tc in environmental samples comprise chemical separation including pre-concentration of ^{99}Tc and removal of matrix components and interferences, and measurement of ^{99}Tc . The sample pre-treatment is a critical step. The release and transfer of ^{99}Tc from solid sample to solution is normally carried out by ashing or alkali fusion followed by acid leaching. Converting all Tc to TcO_4^- is a key step to ensure a successful transfer of Tc to solution because of the high solubility of TcO_4^- compared with other species of Tc. Adjustment of the oxidation state of Tc is also a key step for pre-concentration of Tc from water samples, which is based on the water insolubility of Tc(IV) and high affinity of TcO_4^- on anion exchange resin. Another very important issue is the loss of Tc during the ashing and evaporation steps due to the high volatility of Tc_2O_7 . Ashing of solid samples to remove organic matters should be carried out at a temperature lower than 700°C , and ^{99}Tc solution, especially in HCl medium, should not be evaporated to complete dryness, to avoid significant loss of Tc in these steps. Co-precipitation and anion exchange chromatography are two efficient techniques for pre-concentrating ^{99}Tc from large volumes of water, and from leachates from solid samples, as well as to remove most matrix components from the samples. The formed precipitate, especially carried by CuS or FeS , should be dissolved over short time after separation to avoid the difficulties in redissolving the reduced Tc in the precipitate. Formation of colloids and organisms during water storage may cause a significantly reduced chemical yield of Tc during anion exchange chromatographic separation; this effect can be partly reduced by shortening the storage time and acidifying and poisoning water after collection. Solvent extraction, anion exchange chromatography and extraction chromatography are effective methods for purification of ^{99}Tc from interferences. Of these, solvent extraction and extraction chromatography using TEVA resin are suitable for decontamination of Ru and Mo, the two major interferences in mass spectrometric measurement of ^{99}Tc . To obtain sufficient chemical separation of ^{99}Tc for its determination in low level, a combination of two or more separation techniques are often applied: for example anion exchange or co-precipitation followed by extraction chromatography.

ICP-MS and β counting are two commonly used detection methods for ^{99}Tc . The radiometric method using low level GM counters is easily accessible and cost-effective, but requires relatively long measurement time. ICP-MS is fast and sensitive, but the isobaric and spectrometric interferences to mass 99 are major challenges for obtaining a reliable result. With the development and increased installation of instruments, ICP-MS is becoming a more popular and frequently used technique for ^{99}Tc measurement in low level environmental samples. However, an improvement of chemical separation procedures and experimental conditions is still needed to obtain a better and more stable decontamination of Ru and Mo. The applicability of both β counting with GM counter and ICP-MS can be proven by comparison exercises where the same sample is

measured using the two techniques. Due to short analytical time, less labour, and on-line analytical characterisation, automated analytical methods combining chromatographic separation employing flow/sequential injection with rapid measurement using ICP-MS are becoming more attractive, especially with the requirement of rapid determination of ^{99}Tc in emergency situations and the increased application of ICP-MS and extraction chromatography. Its application is currently limited to a few laboratories. However, with the development of this technique and commercialization of automated separation instruments, it might in a near future become a popular and routine analytical method for determination of ^{99}Tc .

Acknowledgements

K.L. Shi acknowledges the China Scholarship Council for the partial financing of his PhD study at DTU. The authors thank Dr. Kasper Andersson in Risø DTU for his kindly improvement of the English presentation of this article.

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Analytical Chemistry 2012, 84, 2009-2016

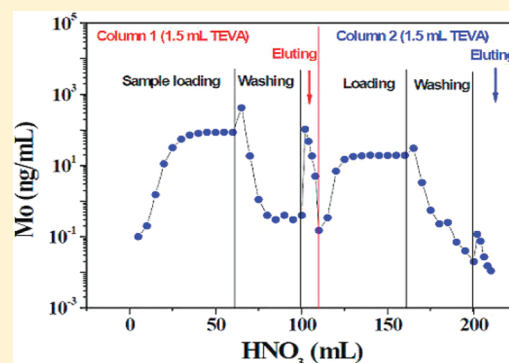
Stability of Technetium and Decontamination from Ruthenium and Molybdenum in Determination of ^{99}Tc in Environmental Solid Samples by ICPMS

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ABSTRACT: A rapid and efficient method for the determination of ^{99}Tc in environmental solid samples was developed using chromatographic separation combined with inductively coupled plasma mass spectrometry (ICPMS) measurement. The volatility of technetium during sample ashing and solution evaporation was investigated to establish a reliable sample pretreatment procedure. A novel approach was developed to improve the removal of molybdenum and ruthenium in chromatographic separation using 30% H_2O_2 pretreatment of the loading solution and extraction chromatographic separation using two serial small TEVA columns. The decontamination factors of more than 4×10^4 and 1×10^5 are achieved for molybdenum and ruthenium, respectively. Chemical yields of technetium in entire procedure range from 60% to 95% depending on the type and amount of samples, and the detection limit of 0.15 mBq/g for ^{99}Tc was obtained. The method has been successfully applied for the determination of ^{99}Tc in environmental solid samples.



Technetium-99 (^{99}Tc) is a long-lived radionuclide with a half-life of 2.13×10^5 years which is produced through thermal neutron fission reactions of ^{235}U (fission yield of about 6%) and ^{239}Pu . In the present environment, ^{99}Tc is mainly released from spent nuclear fuel reprocessing plants and nuclear weapons testing, of which most of the ^{99}Tc (>90%) has been discharged from reprocessing plants in Europe.¹ Because of the long half-life and high mobility (weak sorption of TcO_4^- to geological media), ^{99}Tc has been regarded as one of the most important radionuclides for safety assessment of environmental radioactivity and repository of nuclear waste.² Due to the high solubility of TcO_4^- in seawater, and consequently long residence time of technetium in the oceans, ^{99}Tc is an ideal oceanographic tracer for the study of movement, exchange, and circulation of water masses.^{3,4} In addition, technetium is an artificial element without any stable isotopes and ^{99}Tc is the major radioisotope of technetium. Investigation of the environmental behavior of ^{99}Tc is highly interesting for estimation of its biological effect and health risk. This requires an accurate determination of ^{99}Tc in various environmental samples.

Several methods have been reported for ^{99}Tc determination;^{5–10} these methods generally include sample pretreatment, preconcentration, purification, and measurement of ^{99}Tc . For pretreatment of solid samples such as seaweed, dry ashing is a commonly used but critical step because of the loss of volatile technetium species and incomplete decomposition of organic matter, therefore causing a problem in accurate determination of ^{99}Tc .¹¹ Some studies on the volatility of technetium during sample ashing have been reported,^{6,7,12,13} but the conclusions are contradictory and confusing. The stability of ^{99}Tc in the

sample solution during the evaporation step is also very critical and might cause a significant loss of ^{99}Tc . Matrix elements as well as compounds would presumably affect the volatility of technetium. Systematic investigation on the loss of technetium during evaporation of solution is still scarce, and the reported results in the literature are contradictory.¹⁴

As a pure β -emitter with maximum energy of 0.292 MeV, ^{99}Tc is conventionally measured by β -counting using a gas flow Geiger–Müller (GM) counter or by liquid scintillation counting (LSC).^{6,8,15} However, the relatively high detection limit or long counting time restrict applications of these techniques, especially for analysis of low-level environmental samples and for emergency analysis. Alternatively, inductively coupled plasma mass spectrometry (ICPMS) is a better choice for this purpose.^{7,16–20} It allows rapid measurement of ^{99}Tc with a better sensitivity. In ICPMS measurement of ^{99}Tc , stable ^{99}Ru and the molecular ion $^{98}\text{Mo}^1\text{H}$ are two main isobaric interferences; ^{98}Mo also affects the measurement of ^{99}Tc due to tailing of ^{98}Mo to the mass of 99. These interferences seriously worsen the detection limit for ^{99}Tc and hinder its accurate determination. Several methods such as solvent extraction, ion-exchange chromatography, and extraction chromatography have been employed for removing molybdenum and ruthenium;^{21,22} among these, extraction chromatography using a TEVA column is a commonly used method.^{18,23–25} However, the reported

Received: November 25, 2011

Accepted: January 11, 2012

Published: January 11, 2012



decontamination of molybdenum and ruthenium using this method is still not highly appreciated,²⁴ and other methods such as solvent extraction and ion-exchange chromatography are usually combined to obtain sufficient decontamination factors. These will prolong the analysis time, and some organic waste are also produced.

This work aims to investigate the stability of technetium during dry ashing and evaporation procedures in order to develop reliable methods for sample pretreatment and technetium separation and to explore the behavior of technetium, ruthenium, and molybdenum on TEVA resin to find an efficient approach for sufficient removal of ruthenium and molybdenum for measurement of ^{99m}Tc in low-level environmental samples using ICPMS.

■ EXPERIMENTAL SECTION

Reagents and Materials. ^{99m}Tc tracer was obtained from commercial ⁹⁹Mo–^{99m}Tc generators (3–5 GBq) and purified using alumina cartridges according to the method reported by Hou et al.²⁶ A ⁹⁹Tc standard solution, in the form of NH₄TcO₄ with an activity of 4.17 Bq/g (6.51 ng/g), was supplied by Risø National Laboratory for Sustainable Energy (Denmark). Ruthenium and molybdenum standard solutions with natural isotopic composition were purchased from CPI international Inc. (Berkeley, U.S.A.). All other reagents used in the experiment were of analytical grade and prepared using deionized water (18.2 MΩ·cm⁻¹).

Eichrom TEVA extraction chromatographic resin (100–150 μm particle size) was purchased from TRISKEM International (Bruz, France). Certified reference materials soil (IAEA 375) and seaweed (IAEA 446) were obtained from the Marine Environmental Laboratory of the International Atomic Energy Agency (Monaco), and seaweed standard reference material (NIST-SRM-4359) was supplied by the National Institute of Standards and Technology (Gaithersburg, U.S.A.). A Danish seaweed sample was collected at Klint, Denmark in 2005, air-dried, ground, and sieved through a 50 mesh sieve. The Danish soil sample was collected from 12 locations in Denmark, air-dried, mixed, ground, and sieved through a 100 mesh sieve. These two samples were used for the method development.

Investigation on the Volatility of Technetium during Solution Evaporation. For each experiment, three aliquots of 10 mL of sample solution (in HNO₃, HCl, or NH₃·H₂O media) were prepared in glass beakers. After being spiked with ^{99m}TcO₄⁻, the beakers were placed on a hot plate at a certain temperature (100, 150, and 200 °C) until near dryness (about 0.5 mL left) or dryness. After being cooled to room temperature, the residue was dissolved using 10 mL of 1 mol/L HNO₃ and the solution was transferred to a glass tube for yield measurement using a NaI γ detector. For the investigation of matrix effect, a certain amount of 25 g/L KCl was added to the solution before evaporation.

Investigation on the Stability of Technetium during Dry Ashing. For seaweed samples, different ashing temperatures (650, 700, 750, and 800 °C for 6 h), time (1.5, 3, 6, 14, and 21 h at 700 °C), and pre-conditions (untreated sample, pretreatment with HCl or NH₃·H₂O) were investigated. Three aliquots of 10 g of dried seaweed powder were taken to beakers for each experiment. After being spiked with ^{99m}Tc tracer, the seaweed samples were wetted with NH₃·H₂O (except for the experiments with the different prereagents) and dried on a hot plate, then placed in a muffle furnace; the temperature was increased with a mean rate of 8 °C/min and kept at the

specified temperature for a certain time period. After being cooled to room temperature, ^{99m}Tc in the residues was leached with 10 mL of 8 mol/L HNO₃ and the solution was transferred into a glass tube for yield measurement using a NaI γ detector. For soil samples, different pretreatment methods (untreated sample, pretreatment with HCl or NH₃·H₂O) before ashing were studied. Except for the ashing temperature of 550 °C, similar ashing procedures were followed as for seaweed. After being cooled to room temperature, ^{99m}Tc in the residues was leached with 50 mL of 8 mol/L HNO₃ to measure the yield using a NaI γ detector.

Leaching and Preconcentration of Technetium from Ashed Samples. To the ashed sample, 40 mL of 3 mol/L HCl was added to the residue and the solution was heated on a hot plate at 70–90 °C under reflux for 1.5 h to leach technetium; 10 mL of 30% H₂O₂ was added gradually during leaching. The cooled solution was filtered through a GF/A filter, the filtrate was collected into a centrifuge tube, the crucible and filter paper were washed with 20 mL of 0.1 mol/L HCl solution and the washes were combined with the leachate. An amount of 0.1–0.2 g of Fe (as FeCl₃ solution) was added to the filtrate (no Fe added for soil and sediment samples), and 6 mol/L NaOH was added to adjust the pH to 1. Then 0.5–1.0 g of K₂S₂O₅ was added to reduce TcO₄⁻ to Tc⁴⁺ and Fe³⁺ to Fe²⁺. After mixing, 6 mol/L NaOH is added to adjust to pH 9–10 to coprecipitate Tc⁴⁺ as TcO₂ with Fe(OH)₂. The precipitate was separated by centrifugation at 4000 rpm for 10 min, and the supernatant was discarded.

The precipitate was dissolved with 10 mL of 8 mol/L HNO₃, and 5 mL of 30% H₂O₂ was added to oxidize Tc⁴⁺ to TcO₄⁻. Then 6 mol/L NaOH was added to adjust to pH 9–10, and the solution was centrifuged to remove Fe(OH)₃ with hydroxides of other transition metals in the precipitate. The supernatant containing TcO₄⁻ was transferred to another beaker. To reduce the loss of technetium due to entrapment in the precipitate, the precipitate was dissolved with 5 mL of 8 mol/L HNO₃, and precipitation was carried out again by addition of 6 mol/L NaOH to pH 9–10. After centrifugation, the supernatants were combined for further separation.

For large amounts of soil or sediment samples (e.g., more than 50 g), after ashing and leaching, a precipitation step was followed to remove Fe and other elements easily precipitated from sample matrixes, then 0.1–0.2 g of Fe³⁺ was added, and the same procedures mentioned above were followed.

Separation of Technetium Using Extraction Chromatography. The distribution coefficients (*K_d*, mL/g) of technetium, molybdenum, and ruthenium on TEVA resin in different concentrations of HNO₃ were investigated by batch experiments. An amount of 10 mL of HNO₃ in concentrations of 0.001–10 mol/L containing 100 μg/L MoO₄²⁻ and 10 μg/L RuO₄⁻ was transferred to a 20 mL glass bottle, and 0.2 g of TEVA resin was added to the bottle. The samples were then shaken for 6 h at room temperature and centrifuged at 4000 rpm for 10 min to separate resin and solution. Because of the interference of molybdenum and ruthenium in the ICPMS measurement of ⁹⁹Tc, the batch experiment for technetium was carried out separately. With the difference that the solution only contained 100 ng/L ⁹⁹TcO₄⁻, the other steps were the same as the procedure for molybdenum and ruthenium. Three replicates were performed for each experiment. The concentrations of ⁹⁹Tc, molybdenum, and ruthenium in each solution were measured by ICPMS.

Two small extraction chromatography columns (1.5 mL of each) filled with TEVA resin (100–150 μm) were applied for technetium separation. Before chromatographic separation, 30% H_2O_2 is added to the alkaline supernatant containing ^{99}Tc ; 8 mol/L HNO_3 was then added to adjust pH to 1. After the sample was loaded on the first TEVA column, 40 mL of 1 mol/L HNO_3 was used to wash the column, and technetium on the column was finally eluted with 10 mL of 8 mol/L HNO_3 . The eluate was diluted to 40 mL with water and 6 mol/L NaOH to pH 1 and then loaded on to the second column. The same separation procedure as for the first column was applied for separation of ^{99}Tc . The final eluate (8 mol/L HNO_3) was evaporated to dryness on a hot plate at 70–90 $^\circ\text{C}$. The residue was dissolved in 5 mL of 0.5 mol/L HNO_3 solution, which was measured for $^{99\text{m}}\text{Tc}$ using a NaI γ detector to monitor the chemical yield.

Measurement of ^{99}Tc by ICPMS. One week after separation (for allowing for decay of short-lived $^{99\text{m}}\text{Tc}$ ($t_{1/2} = 6$ h)), indium solution (as $\text{In}(\text{NO}_3)_3$) was added to the separated ^{99}Tc solution to a concentration of 1.0 $\mu\text{g/L}$ as internal standard for instrument calibration. ^{99}Tc in 0.5 mol/L HNO_3 solutions was measured by an ICPMS system (X series, Thermo Fisher Scientific, Waltham, MA) equipped with an Xs skimmer cone and a concentric nebulizer, operated under hot plasma conditions. Prior to sample measurement, the ICPMS

instrument was optimized using ^{99}Tc standard solution (10.0 ng/L); typical response for ^{99}Tc ranged from 1×10^5 to 3×10^5 counts/s per $\mu\text{g/L}$.

A series of ^{99}Tc standard solutions were prepared in 0.5 mol/L HNO_3 containing 1.0 $\mu\text{g/L}$ In^{3+} to calibrate the instrument. A linear regression line was proven over the concentration range of 0.1 to 200 ng/L for ^{99}Tc . A 0.5 mol/L HNO_3 solution was used as rinsing solution among consecutive assays.

The analytical procedure is illustrated in Figure 1, and the important aspects are discussed in the following sections.

RESULTS AND DISCUSSION

Loss of Technetium during Evaporation of the Sample Solution. Evaporation is often used to reduce the sample volume and to remove acids in the sample solution in an analytical procedure of ^{99}Tc . Due to the volatility of technetium, the loss of technetium might happen during evaporation. The volatility of technetium during different evaporation conditions was investigated. The results (Table 1) show that temperature and solution composition are key parameters determining the volatility of technetium during evaporation. No significant loss of technetium was observed when evaporation was carried out at a temperature lower than 100 $^\circ\text{C}$ in HNO_3 media, even in a HNO_3 solution up to 8 mol/L, although technetium becomes volatile when the temperature is increased. At 150 $^\circ\text{C}$, an

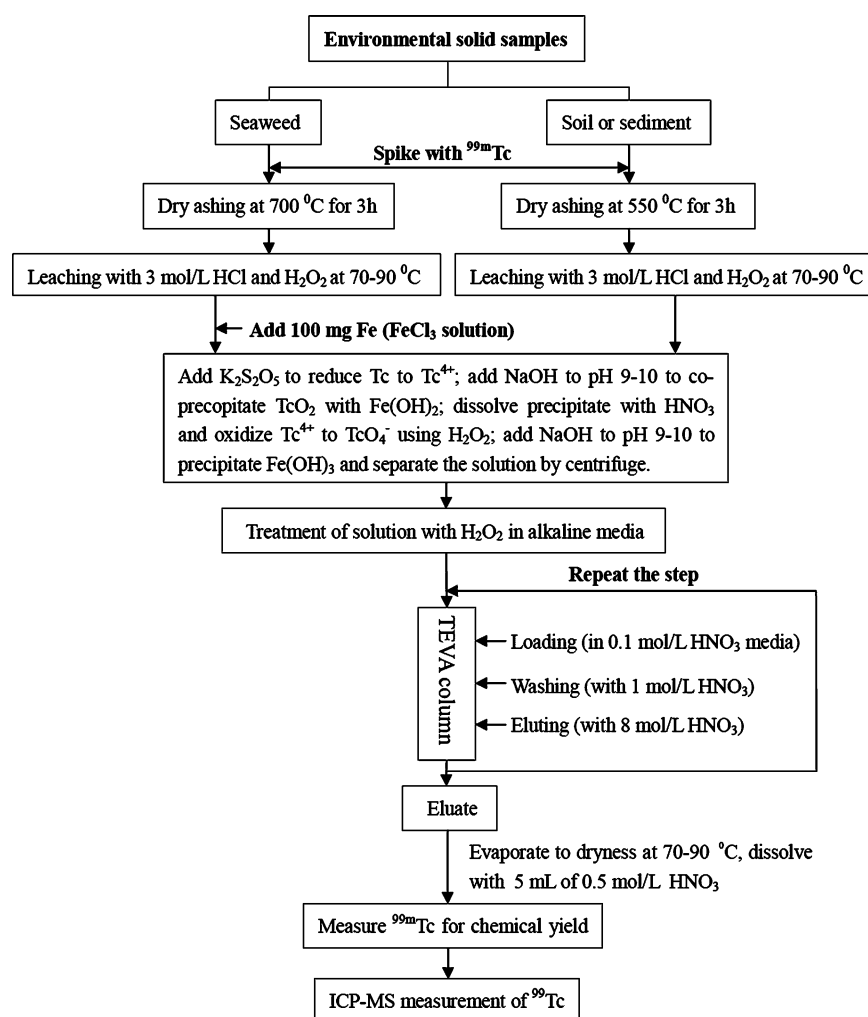


Figure 1. Analytical procedure for the determination of ^{99}Tc in environmental solid samples.

Table 1. Volatility of Technetium in Evaporation of Sample Solution at Different Conditions^a

solution media	yield of Tc at different temperatures on a hot plate (%)			status after evaporation
	100 ± 2 °C	150 ± 2 °C	200 ± 2 °C	
25% NH ₃ ·H ₂ O	97.0 ± 2.1	94.6 ± 1.9	71.1 ± 2.6	dryness
0.001 mol/L HNO ₃	95.8 ± 1.4	94.3 ± 1.8		dryness
0.001 mol/L HNO ₃ with salt	98.7 ± 2.1	99.4 ± 2.5		dryness
0.1 mol/L HNO ₃	99.1 ± 2.4	86.4 ± 2.3		dryness
0.1 mol/L HNO ₃ with salt	98.2 ± 2.3	95.4 ± 2.1		dryness
8 mol/L HNO ₃	98.5 ± 1.9	79.4 ± 2.7	59.5 ± 3.9	dryness
8 mol/L HNO ₃ with salt	100.5 ± 2.3	96.3 ± 3.0	70.6 ± 3.3	dryness
0.001 mol/L HCl	90.2 ± 2.1	65.1 ± 3.7		dryness
0.001 mol/L HCl with salt	98.4 ± 1.9	103.2 ± 4.6		dryness
0.1 mol/L HCl	79.2 ± 2.0	53.1 ± 1.9		dryness
0.1 mol/L HCl with salt	94.1 ± 2.1	72.7 ± 1.1		dryness
3 mol/L HCl	32.2 ± 2.3	10.7 ± 4.1		dryness
3 mol/L HCl with salt	84.1 ± 1.9	53.9 ± 3.6		dryness
6 mol/L HCl	1.3 ± 0.3	1.8 ± 0.2	1.5 ± 0.4	dryness
3 mol/L HCl with H ₂ O ₂	37.2 ± 1.8	13.2 ± 3.2		dryness
3 mol/L HCl with salt	99.1 ± 2.3	88.8 ± 1.5		0.5 mL of solution left
3 mol/L HCl with H ₂ O ₂	97.4 ± 2.6	72.9 ± 3.1	65.2 ± 3.4	0.5 mL of solution left
8 mol/L HNO ₃	98.5 ± 1.7	97.1 ± 2.6		0.5 mL of solution left

^aThe yields are presented as the average and 2SD of three replicates.

increased loss of technetium was observed with increasing HNO₃ concentration from less than 5% in 0.001 mol/L HNO₃ to more than 20% in 8 mol/L HNO₃. This might be attributed to the formation of volatile species of technetium, Tc₂O₇ (melting point of 119 °C), in high concentration of HNO₃ and at high temperature. In high concentration of acid, HTcO₄ is easily formed, which is converted to Tc₂O₇ by dehydrolysis when the solution is evaporated to dryness; the formed Tc₂O₇ is easily lost due to its high volatility. It has been proposed that changing the solution to alkaline media can reduce the loss of technetium during evaporation process;²⁷ this is because TcO₄⁻ is much more stable in alkaline conditions.¹⁴ Our results showed the same stability of technetium in 25% NH₃·H₂O as in diluted HNO₃ solution (0.001 mol/L). However, when the temperature increased to 200 °C, a significant loss of technetium was observed. This might be explained as when the solution is evaporated to dryness, all excessive NH₃·H₂O is removed, and at high temperature NH₄TcO₄ could be converted to Tc₂O₇ to some extent and lost.

The addition of salt in solution can significantly reduce the loss of technetium in the evaporation process. In 10 ml of 8 mol/L HNO₃ media with 25 g/L KCl, no significant loss of technetium was observed when the solution was evaporated to dryness at 150 °C, compared with more than 20% loss of technetium when no KCl was added. This might be explained as that technetium can attach to or be enwrapped in the formed salt crystals when the solution was evaporated to dryness, isolating technetium from the high-temperature bottom of the beaker, which consequently reduced the temperature directly

surrounding the TcO₄⁻. In addition, the formation of less volatile KTcO₄ instead of HTcO₄ (Tc₂O₇) when the solution was evaporated to dryness might be another reason.

Technetium is highly unstable in HCl media during evaporation, even at 100 °C and in 0.001 mol/L HCl solution. The loss of technetium significantly increases with the increased concentration of HCl; more than 98% of technetium was lost when evaporation was carried out in 6 mol/L HCl at 100 °C. It has been reported that TcO₄⁻ could be reduced to a low oxidation state in high concentration of HCl.^{28,29} To confirm if high loss of technetium in the increased concentration of HCl is attributed to the formation of highly volatile low oxidation state species of technetium, 30% H₂O₂ was added to technetium solution in 3 mol/L HCl medium before evaporation, but similar high losses of technetium for solution with H₂O₂ (63%) and without H₂O₂ (67%) were obtained (Table 1) when evaporated to dryness at 100 °C. This could not only be explained by the formation of Tc₂O₇ because no significant loss of technetium was observed in the high-concentration HNO₃ solution when evaporated at 100 °C. A more likely explanation is the formation of some volatile complexes of technetium with Cl⁻ in HCl media.

It is interesting that no significant loss of technetium was observed if the solution was not evaporated to complete dryness (about 0.5 mL solution left) at less than 100 °C even in HCl media. This indicates that the loss of technetium mainly happened after the solution is evaporated to dryness. This phenomenon might be explained by that HTcO₄ or a complex of technetium with Cl⁻ is relatively stable in solution. When the solution is removed, the formed HTcO₄ or complex of technetium with Cl⁻ is decomposed and forms more volatile the species such as Tc₂O₇. In addition, the temperature applied to technetium species is also increased when evaporated to dryness compared with in the solution, which enhances the volatility of the formed species of technetium. On the basis of this finding, it is recommended that technetium solution should be evaporated in HNO₃ or alkali media at lower temperature (<150 °C), and the solution should not be evaporated to complete dryness if the temperature is more than 100 °C.

Loss of Technetium in Sample Ashing. Dry ashing is a preferred method to decompose organic matters in solid samples. However, at high temperature technetium might be lost from the sample through formation of the volatile technetium anhydride (Tc₂O₇), the product of dehydrating pertechnetonic acid (HTcO₄) during heating.^{6,28} For a solid sample, especially biological samples such as seaweed, it is critical to completely decompose the organic substances, which account for 80–90% of the total sample weight. This is due to that technetium might associate with organic compounds in the biological samples, which cannot be completely leached out from the undecomposed samples, and the soluble organic technetium complex might have different behavior compared to inorganic technetium species. A poor chemical yield usually is obtained if the sample is not ashed completely. The reported volatility of technetium during sample ashing is varying, or even is contradictory. Harvey et al.²⁸ reported a significant loss of ⁹⁹Tc when seaweed samples were ashed around 550 °C, whereas other authors^{7,30} have reported that no apparent loss of ⁹⁹Tc was observed when the seaweed sample was ashed below 800 °C. Some literature reports that the loss of technetium can be reduced by addition of concentrated HCl to the samples before ashing,¹² although an opposite result has also been reported.⁶ In this work, we investigated the effects of different parameters

influencing the volatility of technetium during sample ashing, including (i) temperature, (ii) time, (iii) pretreatment methods, and (iv) sample matrixes.

The results (Table 2) show that no significant loss of technetium was measured for seaweed when the ashing temperature

Table 2. Volatility of Technetium in Dry Ashing of Seaweed and Soil Samples at Different Conditions^a

sample types	pretreatment	ashing temperature (°C)	ashing time (h)	yield (%)
seaweed	NH ₃ ·H ₂ O	650	6	98.0 ± 2.1
seaweed	NH ₃ ·H ₂ O	700	6	101.7 ± 2.5
seaweed	NH ₃ ·H ₂ O	750	6	97.9 ± 2.4
seaweed	NH ₃ ·H ₂ O	800	6	100.1 ± 3.1
seaweed	NH ₃ ·H ₂ O	700	1.5	98.9 ± 2.9
seaweed	NH ₃ ·H ₂ O	700	3	97.5 ± 2.1
seaweed	NH ₃ ·H ₂ O	700	6	96.5 ± 2.5
seaweed	NH ₃ ·H ₂ O	700	14	101.9 ± 2.0
seaweed	NH ₃ ·H ₂ O	700	21	87.1 ± 1.9
seaweed	HCl	700	3	93.6 ± 2.8
seaweed	NH ₃ ·H ₂ O	700	3	101.4 ± 3.1
seaweed	untreated	700	3	102.8 ± 3.0
soil	HCl	550	3	75.5 ± 1.5
soil	NH ₃ ·H ₂ O	550	3	100.6 ± 1.0
soil	untreated	550	3	97.1 ± 1.8

^aThe yields are presented as the average and 2SD of three replicates.

was lower than 800 °C. Since the organic component of the seaweed could not be completely incinerated if the temperature is below 650 °C, ashing at 700 °C was selected for further investigation. Ashing duration is not very sensitive for the volatility of technetium during the ashing process; no apparent loss of technetium was observed when ashing for less than 14 h at 700 °C, and about 13% of technetium was lost when the ashing process was extended to 21 h (Table 2). Since organic substances of the seaweed sample could not be completely decomposed in less than 3 h even at 700 °C, a shortest ashing duration of 3 h at 700 °C was selected for further investigations, which is shorter than the reported value of more than 6 h.¹² Our experiments show that the pretreatment of seaweed samples with 25% NH₃·H₂O does not express any difference in the yield of ⁹⁹Tc during the ashing process compared with the sample untreated; both conditions do not show any significant loss of technetium when ashing at 700 °C for 3 h. However, a slightly lower yield of ⁹⁹Tc (94%) was observed when the sample was pretreated with concentrated HCl (Table 2). This might be attributed to the formation of volatile Tc₂O₇ or technetium complex with Cl⁻ when HCl is added, which converts TcO₄⁻ to HTcO₄ and further to Tc₂O₇ at high temperature.

For soil samples, because of the relatively low level of organic matter, sample ashing at 550 °C for 3 h is enough to remove the organic matter. Different pretreatment methods before ashing were investigated, and results (Table 2) show that no significant difference of technetium losses was observed when the soil samples were pretreated with NH₃·H₂O or not. However, about 25% of technetium is lost if the sample was pretreated with concentrated HCl, which is about 5 times higher than that for seaweed. This can be explained by that the composition of these two kinds of samples is different. Highly unstable species of technetium might be formed when the soil sample is pretreated with concentrated HCl.

Although the same high yield of technetium can be obtained regardless of sample pretreatment with NH₃·H₂O or not, it was noticed that the sample became fluffy and easier to completely ash at the same temperature and duration if the sample was pretreated with NH₃·H₂O. The pretreatment of the sample with NH₃·H₂O before ashing is therefore recommended, especially for seaweed samples.

Decontamination of Molybdenum and Ruthenium.

For ⁹⁹Tc measurement by ICPMS, the main challenges are the isobaric interferences at 99 amu. Among these, the stable isotope ⁹⁹Ru and the molecular ion ⁹⁸Mo¹H are the main interferences which need to be removed sufficiently before measurement.¹¹ In this work, extraction chromatography using TEVA resin was investigated for the removal of molybdenum and ruthenium.

The sorption kinetics of TcO₄⁻, MoO₄²⁻, and RuO₄⁻ on TEVA resin have been investigated (not shown here). It was found that the uptake process of them on TEVA is rapid and an equilibrium state can be reached within 30 min. The distribution coefficients (*K_d*) of these nuclides as a function of concentration of HNO₃ has been measured using a sorption time of 6 h at room temperature (Figure 2). Compared with

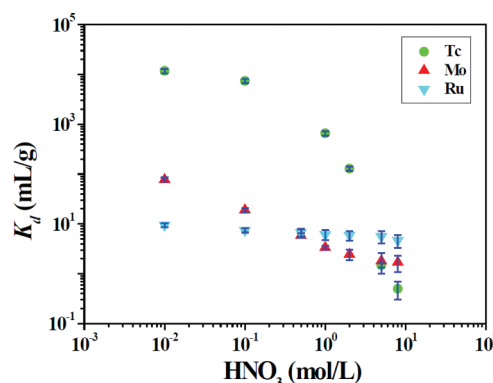


Figure 2. Distribution coefficients of TcO₄⁻, MoO₄²⁻, and RuO₄⁻ on TEVA resin as a function of HNO₃ concentration, obtained at room temperature following an equilibrium time of 6 h. The average and 2σ (standard deviation) of results of three replicates are shown.

MoO₄²⁻ and RuO₄⁻, high sorption of TcO₄⁻ on TEVA resin was observed at low concentration of HNO₃; for example, the *K_d*_{Tc} > 1000 for [HNO₃] < 1 mol/L. The *K_d* of TcO₄⁻ on the TEVA resin decreases rapidly with increased HNO₃ concentration. When the HNO₃ concentration is higher than 4 mol/L, the *K_d* of TcO₄⁻ is lower than that of MoO₄²⁻ and RuO₄⁻ (Figure 2). MoO₄²⁻ also shows a decreased *K_d* with increased HNO₃ concentration, while the *K_d*_{Mo} is still high in low concentrations of HNO₃ (e.g., *K_d*_{Mo} > 100 for [HNO₃] < 0.01 mol/L). In order to remove molybdenum but keep technetium on the column, a loading solution in 0.1 mol/L HNO₃ and washing solution of 1 mol/L HNO₃ were selected. Although a relatively low *K_d* (<10) of RuO₄⁻ on TEVA resin was observed, it does not obviously vary with HNO₃ concentration. This means that the adsorbed RuO₄⁻ is not easily removed from the TEVA column by washing with HNO₃ in a higher concentration.

Chromatographic separation of technetium from molybdenum has been carried out using a 1.5 mL TEVA column (7 mm in diameter and 40 mm in height) by loading sample solution in 0.1 mol/L HNO₃, washing with 40 mL of 1.0 mol/L HNO₃, and eluting with 10 mL of 8 mol/L HNO₃; the results (Figure 3) show

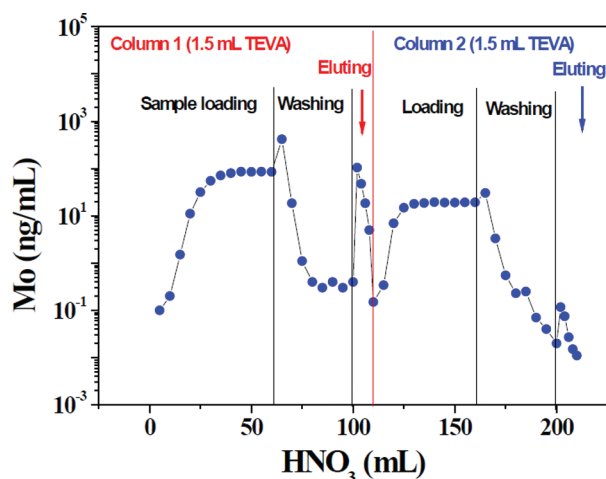


Figure 3. Sorption and elution behavior of molybdenum on a TEVA column (sample, 10 g of Danish seaweed; flow rate, 1.0–1.2 mL/min; loading solution, in 0.1 mol/L HNO_3 media; washing solution, 1 mol/L HNO_3 ; eluting solution, 8 mol/L HNO_3).

that some amount of molybdenum still is present in the eluate of technetium; a decontamination factor for molybdenum by this process is less than 300. This is attributed to the relatively high K_d value of MoO_4^{2-} in low concentration of HNO_3 media (Figure 2), such as 0.1 mol/L HNO_3 , reflected in the low molybdenum concentration in the first 25 mL of effluent in Figure 3. The absorbed molybdenum on the column could not be efficiently removed by 1 mol/L HNO_3 due to the still relatively high K_d value of MoO_4^{2-} in 1 mol/L HNO_3 . The remaining molybdenum is finally eluted with technetium to the eluate, reflected by a relative high molybdenum concentration in the eluate (Figure 3). Chromatographic separation using one TEVA column (1–2 mL) seems not sufficient to remove molybdenum. Two serial TEVA columns (2×1.5 mL) were tested to improve the decontamination of molybdenum. The eluate from the first TEVA column was diluted with deionized water and 6 mol/L NaOH to a HNO_3 concentration of 0.1 mol/L and then loaded to the second TEVA column to separate technetium using the same procedure as the first column. The results (Figure 3) show that the molybdenum concentration in the eluate from the second column is reduced by 2 orders of magnitude compared with the eluate from the first column, and the overall decontamination factor of molybdenum reaches more than 4×10^4 . By this way, the interference of molybdenum can be sufficiently suppressed.

Although RuO_4^- has a low K_d value (<10) in low HNO_3 concentration, the $K_{d,\text{Ru}}$ does not vary with HNO_3 concentration; consequently, the absorbed ruthenium cannot be easily removed from the TEVA column. Even with two serial TEVA columns, some ruthenium still can be observed in the final eluate, and it is difficult to obtain a sufficiently high decontamination for ruthenium. This will interfere with the ICPMS measurement of ^{99}Tc and prevents sufficient low detection limits for ^{99}Tc . A few methods have been reported to remove ruthenium from technetium; on the basis of the high volatility of RuO_4 , ruthenium is removed from sample solution by oxidizing with strong oxidant and heating at high temperature in H_2SO_4 media.^{21,31} This method is simple but quite time-consuming and may results in losses of ^{99}Tc at high temperature; the decontamination factor of ruthenium only by this step is still not sufficiently high. It has been reported that RuO_4^- can be reduced to a lower oxidation state by 30% H_2O_2

in alkaline media.³¹ The reduced ruthenium in Ru^{4+} or Ru^{3+} could not form an anion in HNO_3 , especially in a low concentration of HNO_3 . An experiment was carried out to investigate the effect of treating the loading solution with 30% H_2O_2 in different media with respect to removal of ruthenium using a TEVA column. The results (Table 3) show that the

Table 3. Effect of Pretreatment of Sample Solution with 30% H_2O_2 in Different Media with Respect to Removal of Ruthenium by Extraction Chromatography Using a 1.5 mL TEVA Column^a

chromatographic step	vol of effluent/ washes (mL)	concn of Ru in the effluent or washes with different pretreatments of the loading solution ($\mu\text{g/L}$)		
		pretreatment with H_2O_2		untreated
		1 mol/L NaOH	H_2O	
effluent (in 0.1 mol/L HNO_3)	0–4	0.131	0.102	0.070
	4–8	0.197	0.150	0.091
	8–12	0.197	0.159	0.089
	12–16	0.196	0.154	0.092
	16–20	0.195	0.154	0.089
washing (1 mol/L HNO_3)	0–4	0.067	0.054	0.045
	4–8	<0.001	0.004	0.003
	8–12	<0.001	0.004	0.002
	12–16	<0.001	0.005	0.002
	16–20	<0.001	0.005	0.003
relative amount of Ru in both effluent and washes compared with the original amount of Ru in the loading solution		98%	79%	49%

^aAfter pretreated using 30% H_2O_2 in 1 mol/L NaOH and H_2O , the solution was acidified to pH 1 with HNO_3 before loading; as comparison, the results for Ru in 0.1 mol/L HNO_3 (without treatment using 30% H_2O_2) are also listed.

treatment of the loading solution with H_2O_2 in 1 mol/L NaOH media can significantly reduce the adsorption of ruthenium on the TEVA column, and more than 98% of ruthenium in the loading solution is removed to the effluent and 1 mol/L HNO_3 washes. As a comparison, the treatment with H_2O_2 in neutral media (in H_2O) and no treatment result in a removal of ruthenium of only 79% and 49%, indicating that ruthenium might be effectively reduced to a low oxidation state by H_2O_2 in alkaline media and therefore significantly reduce the absorption of ruthenium on the TEVA column. By this approach, the decontamination factor of more than 1×10^5 for ruthenium is achieved.

Detection Limit of the Established Method. With the sufficient removal of molybdenum and ruthenium using the developed procedure, a detection limit of 0.15 mBq/g (0.23 pg/g) for 10 g seaweed or soil has been obtained using ICPMS (X-series II, Thermo Scientific) in our experiment (based on the 3 times of the standard deviation of signal of the procedure blank), which is several times lower than the reported values obtained by ICPMS (1 mBq/g)⁷ or radiometric method using LSC (1.7 mBq/g).⁶ Therefore, the developed analytical procedure can be used for the determination of ^{99}Tc in low-level environmental samples.

Separation Capability of the Analytical Procedure. Although several methods have been reported for the determination of ^{99}Tc in environmental samples, yet only a

Table 4. Investigation on the Separation Capability of the Analytical Procedure^a

samples (Danish soil)	⁹⁹ Tc spiked (Bq/kg)	chemical yield (%)	⁹⁹ Tc measured (Bq/kg)	decontamination factors	
				Mo	Ru
10 g	45.71 ± 0.09	78–85	46.71 ± 1.19	(4.4 ± 0.3) × 10 ⁴	(1.0 ± 0.2) × 10 ⁵
100 g	4.57 ± 0.01	65–75	4.51 ± 0.12	(2.5 ± 0.2) × 10 ⁵	(1.1 ± 0.1) × 10 ⁵
500 g	0.91 ± 0.01	60–68	0.89 ± 0.06	(1.2 ± 0.1) × 10 ⁶	(5.1 ± 0.3) × 10 ⁵

^aResults are given as the average and 2SD of three replicates.

few methods for analysis of large solid samples (e.g., soil and sediment) of more than 50 g are available.^{6,9,20,32} Concentrations of ⁹⁹Tc in environmental samples ranges widely depending on the sample types, sampling location, and sources of ⁹⁹Tc. For soil samples, especially those exposed to only global fallout, a large sample of more than 100 g is required when measured by low-level β -counting or ICPMS.

To explore the separation capability of the developed method, Danish soil samples of 10–500 g were analyzed. To evaluate the analytical quality, the standard addition method was applied by spiking a known amount of ⁹⁹Tc standard solution to the sample before analysis. The results (Table 4) show a good agreement between the measured ⁹⁹Tc and the spiked values, although slightly reduced recoveries of 60–75% were obtained for 100–500 g soil samples, compared with a recovery of 85% for only 10 g of soil. The increased decontamination factors of ruthenium and molybdenum with the increased sample amount (Table 4) might be attributed to the increased amount of molybdenum and ruthenium in the leachate from the larger sample; this phenomenon is often observed in the separation of trace amount of interferences. These results indicate that the developed method can be used to analyze up to 500 g soil/sediment samples with a high analytical quality.

Analysis of Environmental Samples. To evaluate the accuracy of the developed analytical method for environmental samples with different levels of ⁹⁹Tc, three standard reference materials (IAEA-375 soil, IAEA-446 seaweed, and NIST-4359 seaweed) and a reference sample (Danish seaweed) were analyzed. The analytical results (Table 5) show that the

Table 5. Analytical Results of ⁹⁹Tc in Standard Reference Materials and Environmental Samples Using the Developed Method^a

sample	chemical yield (%)	⁹⁹ Tc measured (Bq/kg)	reference value of ⁹⁹ Tc (Bq/kg)
NIST-4239 (seaweed)	65–69	24.0 ± 1.2	17–48 ^b
IAEA-375 (soil)	60–70	0.23 ± 0.08	0.25 ± 0.02 ^b
IAEA-446 (seaweed)	73–77	14.1 ± 0.7	16 ± 2 ^c
Danish seaweed	85–95	74.8 ± 3.8	70–75 ^c

^aResults are given as the average and 2SD of three replicates.

^bInformation values for a range provided in the certification of the standard reference material. ^cValues determined by a method using solvent extraction plus anion-exchange chromatography for separation and low-level β -counting for measurement.

measured ⁹⁹Tc concentrations in all reference materials and reference samples agree well with the certified values or values determined by other methods, indicating the developed analytical method using two small TEVA columns is an appealing approach for the determination of ⁹⁹Tc in environmental solid samples.

CONCLUSIONS

On the basis of the work presented above, the following conclusions can be drawn out: (1) No significant loss of technetium was observed during ashing of seaweed under 800 °C for less than 6 h. The optimal conditions for seaweed ashing are at 700 °C for 3 h. (2) Evaporation of a solution in different concentrations of HNO₃ to dryness at less than 100 °C does not cause obvious loss of technetium. A significant loss of technetium happens in HCl media, especially in high-concentration HCl, but if a small volume of solution (more than 0.5 mL) remained after evaporation, the loss of technetium can be highly reduced. (3) Pretreatment of loading solution with 30% H₂O₂ in alkaline media can significantly improve the removal of ruthenium in chromatographic separation using a TEVA column; this might be attributed to the reduction of ruthenium in this process. (4) By employing two 1.5 mL TEVA columns, a sufficiently high removal of isobaric interferences of molybdenum and ruthenium can be achieved, and a detection limit of 0.15 mBq/g for ⁹⁹Tc in 10 g of soil or seaweed was obtained using the developed separation procedure and ICPMS measurement. (5) The developed analytical method was proved to be reliable and can be used to determine low-level ⁹⁹Tc in environmental samples.

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ACKNOWLEDGMENTS

K. Shi appreciates the staff in the Radioecology and Tracers Programme (headed by Sven P. Nielsen), DTU Nutech, Denmark for their help during the experiment, as well as the China Scholarship Council for the partial financial support to his Ph.D. project.

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Paper III

Shi, K.L.; Qiao, J.X.; Wu, W.S.; Roos, P.; Hou, X.L.

Rapid determination of technetium-99 in large volume seawater samples using sequential injection extraction chromatographic separation and ICP-MS measurement.

Analytical Chemistry 2012, 84, 6783-6789

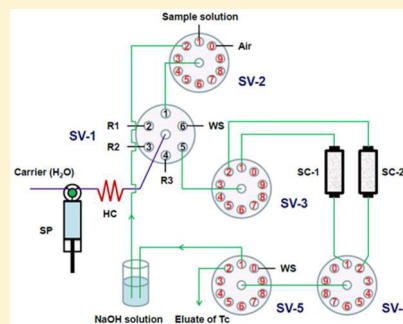
Rapid Determination of Technetium-99 in Large Volume Seawater Samples Using Sequential Injection Extraction Chromatographic Separation and ICP-MS Measurement

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ABSTRACT: An automated method was developed for rapid determination of ^{99}Tc in large volume seawater samples. The analytical procedure involves preconcentration of technetium with coprecipitation, online separation using extraction chromatography (two TEVA columns) implemented in a sequential injection setup, and measurement of ^{99}Tc by inductively coupled plasma mass spectrometry (ICP-MS). Chromatographic behaviors of technetium, molybdenum, and ruthenium were investigated, and the mechanism of adsorption and elution of TcO_4^- on a TEVA column using HNO_3 was explored. The results show that not only NO_3^- but also acidity (or concentration of H^+) of the loading or eluting solution affect the adsorption and desorption of TcO_4^- on TEVA resin. Decontamination factors of more than 1×10^6 for ruthenium and 5×10^5 for molybdenum are achieved. Chemical yields of technetium in the overall procedure range from 60% to 75% depending on the sample volumes, and a detection limit of 7.5 mBq/m^3 (or 11.5 pg/m^3) for 200 L of seawater was obtained. Compared with the conventional analytical procedure, the developed method significantly reduces analytical time. A batch of samples ($n > 4$) can be analyzed within 24 h. The method has been successfully applied for rapid and automated determination of low level ^{99}Tc in large volume seawater samples. The analytical results of seawater samples collected in Denmark show a good agreement with the values obtained using the conventional method.



Technetium-99 (^{99}Tc) is a pure β -emitter with a long half-life of 2.13×10^5 y. It is mainly produced through thermal neutron fission of ^{235}U (fission yield of 6.1%) and ^{239}Pu (fission yield of 5.9%) and is primarily released to the environment from spent nuclear fuel reprocessing plants and nuclear weapons testing.^{1,2} Actually, most of the ^{99}Tc (>90%) in the environment results from the marine discharges of reprocessing plants in Europe.³

In open seas, technetium is mainly present as highly soluble pertechnetate anion, TcO_4^- , which has a low ability to adsorb on particulate matter.⁴ Because of the long half-life of ^{99}Tc as well as high mobility of TcO_4^- in the oceans, ^{99}Tc has been widely employed as an oceanographic tracer to study the exchange and circulation of water masses.^{5–10} Therefore, accurate and rapid determination of ^{99}Tc in seawater is needed.

Because of the extremely low concentration of ^{99}Tc in seawater ($<2 \text{ mBq/m}^3$ in not directly contaminated seas),^{11,12} determination necessitates enrichment and separation of technetium from the sample matrix prior to instrumental measurement. Several techniques such as anion exchange chromatography,¹³ activated carbon sorption,¹⁴ and coprecipitation¹¹ have been used to preconcentrate ^{99}Tc from large volume water samples. Because of the high affinity of TcO_4^- to anion exchange resin, chromatographic techniques using anion exchange columns have been widely applied for separation of technetium from the sample matrix. However, the column might be blocked by the formation of colloids or suspended

substances when the water sample is stored for a long time, causing a low chemical yield or failure of separation. The relatively long pretreatment time (>20 h for a 200 L water sample) is another drawback of the anion exchange chromatographic method that requires spiking of additional tracer if $^{99\text{m}}\text{Tc}$ ($T_{1/2} = 6.06 \text{ h}$) is used as a yield monitor, which might raise the background of ^{99}Tc due to the decay of $^{99\text{m}}\text{Tc}$ to ^{99}Tc . Activated carbon sorption can be used to preconcentrate ^{99}Tc from large volume water samples in a relatively short time, but the following transfer of the absorbed technetium from the sorbent into solution is difficult and requires additional steps such as dry ashing or combustion, which prolongs the analytical time. Coprecipitation is a simple and rapid method to preconcentrate technetium from water, especially suitable for pretreatment of water samples in the field (or on board a sampling vessel), which avoids the problem of transporting large volume water samples back to the home laboratory.⁵ Ferrous hydroxide is often used as a carrier to coprecipitate technetium from sample solutions after reducing technetium to Tc^{4+} . However, to obtain a high enrichment factor of technetium, a large amount of iron is often added; consequently, a bulky iron hydroxide precipitate is formed, which might cause some problems in the following separation

Received: May 15, 2012

Accepted: June 21, 2012

Published: June 21, 2012

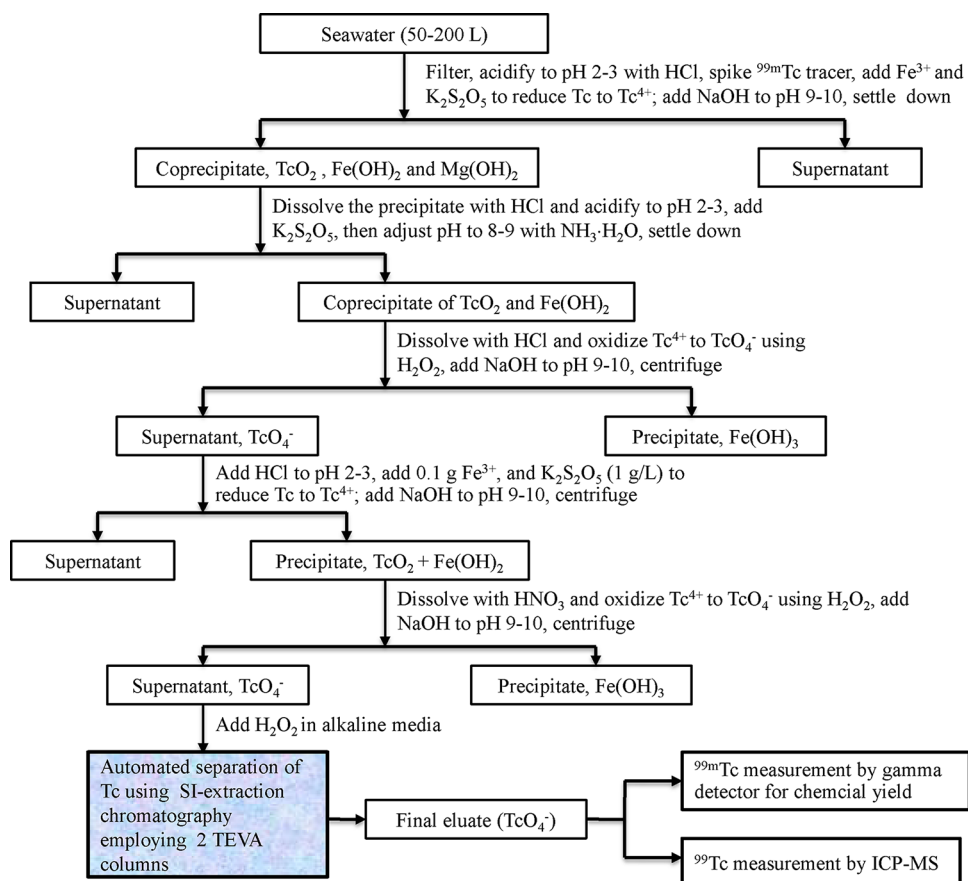


Figure 1. Diagram of chemical procedure for preconcentration and chromatographic separation of technetium from large volume of seawater.

stages, such as difficulties in dissolving the precipitate with a small volume of acid.¹⁵ In addition, the reported coprecipitation methods are not widely used because of low chemical yield of technetium in most cases.¹¹ Accordingly, a relatively rapid and reliable preconcentration method for determination of ⁹⁹Tc in large volume water samples is needed.

As a pure β -emitter, ⁹⁹Tc is usually measured by a low level gas flow Geiger-Müller (GM) counter or liquid scintillation counting (LSC).^{13,16} However, the relatively long counting time (several days for gas flow GM counter) or high detection limit (10–100 pg ⁹⁹Tc for LSC) restricts the application of these techniques,² especially for emergency analysis and measurement of a large number of samples with low levels of technetium. Alternatively, inductively coupled plasma mass spectrometry (ICP-MS) has been successfully applied for rapid detection of ⁹⁹Tc in environmental samples.^{17–19} In ICP-MS measurement of ⁹⁹Tc, stable ⁹⁹Ru and ⁹⁸Mo (via molecular ion ⁹⁸Mo¹H) are the two main sources of interference and have to be sufficiently removed prior to ⁹⁹Tc measurement. Several methods such as solvent extraction, ion exchange chromatography, and extraction chromatography have been applied for elimination of molybdenum and ruthenium, among which extraction chromatography using a TEVA column is an often used method.^{17,19}

Although the conventional methods for determination of ⁹⁹Tc are normally accurate and sensitive, most of them are operated manually and are therefore time-consuming and labor-intensive. Over the past several years, attention has been paid to develop automated methods employing extraction chromatography for determination of radionuclides such as plutonium

based on the flow injection and sequential injection approaches.^{20,21} However, automated analysis of technetium in environmental samples is still scarce and just a few works have been reported.^{22,23} Besides, these reported methods are mainly used for analysis of small size samples, for example 3–6 g of soil,²³ 14 mL of seawater,²⁴ or 1 mL of nuclear waste solution.²² For analysis of large volumes of water, the reported methods might be not reliable because of a large amount of interfering elements in the sample solution after ⁹⁹Tc enrichment.

In this work, we aim to develop a rapid and simple method for preconcentration and separation of technetium from large volume seawater samples to measure ⁹⁹Tc using ICP-MS. For this purpose, a method using coprecipitation with Fe(OH)₂ for enrichment of technetium is optimized and an automated setup for separation of technetium using sequential injection extraction chromatography (two TEVA columns) is established.

■ EXPERIMENTAL SECTION

Reagents and Materials. A ⁹⁹Tc standard solution, in the form of NH₄TcO₄ with an activity of 4.17 Bq/g (6.51 ng/g), was supplied by the Risø National Laboratory, Technical University of Denmark. ^{99m}Tc tracer was obtained from 2 to 4 GBq commercial ⁹⁹Mo–^{99m}Tc generators (Amersham, UK) and purified using alumina cartridges according to the method reported by Hou et al.²⁵ All other reagents used in the experiment were of analytical grade and prepared using deionized water (18.2 MΩ·cm).

Eichrom TEVA (TEtraValent Actinides) extraction chromatographic resin (100–150 μm particle size) was purchased from TrisKem International (Bruz, France). Seawater samples, collected at Roskilde Fjord (Roskilde, Denmark) and Klint (55°58'N, 11°34'E, Kattegat, Denmark) in 2011, were used for the method development.

Preconcentration of Technetium. A filtered seawater sample (50–200 L) was spiked with $^{99\text{m}}\text{Tc}$ tracer (about 500 Bq) and acidified to pH 2–3 using concentrated HCl. After addition of 0–1.6 g of Fe^{3+} (as FeCl_3 solution), $\text{K}_2\text{S}_2\text{O}_5$ (1 g/L seawater) was used to reduce TcO_4^- and Fe^{3+} to Tc^{4+} and Fe^{2+} , respectively, and 6 mol/L NaOH was added to coprecipitate Tc^{4+} as TcO_2 with $\text{Fe}(\text{OH})_2$ and other hydroxides (mainly $\text{Mg}(\text{OH})_2$). After the precipitate was settled by gravity for 6–8 h, the supernatant was discarded, the remaining slurry was dissolved using concentrated HCl, and then 20–50 g of $\text{K}_2\text{S}_2\text{O}_5$ was added to maintain technetium at Tc^{4+} . $\text{NH}_3\cdot\text{H}_2\text{O}$ was added to adjust the pH to 8–9 to coprecipitate TcO_2 with $\text{Fe}(\text{OH})_2$. After the supernatant was discarded, the precipitate was dissolved with concentrated HCl, and 30 mL of 30% H_2O_2 was added to oxidize Tc^{4+} and Fe^{2+} to TcO_4^- and Fe^{3+} , respectively. The sample solution was then diluted to 1 L with deionized water, and 6 mol/L NaOH was added to adjust the pH to 9–10 to remove Fe^{3+} as $\text{Fe}(\text{OH})_3$ precipitate. The supernatant, containing TcO_4^- , was acidified to pH 2–3 with concentrated HCl, and then 0.1–0.2 g of Fe^{3+} (as FeCl_3 solution) and 5 g of $\text{K}_2\text{S}_2\text{O}_5$ were added to the solution to reduce technetium to Tc^{4+} . NaOH (6 mol/L) was added to adjust the pH to 9–10, and the formed coprecipitate of TcO_2 with $\text{Fe}(\text{OH})_2$ was separated by centrifuging at 4000 rpm for 10 min.

The precipitate was dissolved with 10 mL of 8 mol/L HNO_3 , and 5 mL of 30% H_2O_2 was added to oxidize Tc^{4+} to TcO_4^- . Then 6 mol/L NaOH was added to adjust the pH to 9–10, and the formed $\text{Fe}(\text{OH})_3$ precipitate was removed by centrifugation. The supernatant containing TcO_4^- was transferred to a glass beaker. To reduce the loss of technetium enwrapped in the precipitate, the precipitate was dissolved with 5 mL of 8 mol/L HNO_3 and reprecipitated again by addition of 6 mol/L NaOH to adjust the pH to 9–10. The supernatant in two precipitation steps was combined, 5 mL of 30% H_2O_2 was added to reduce ruthenium to its low oxidation state, and the sample solution was finally acidified using 8 mol/L HNO_3 to 0.1 mol/L HNO_3 for further separation of technetium using extraction chromatography. Figure 1 shows a schematic diagram of the preconcentration procedure.

Separation and Purification of Technetium. An automated system based on the sequential injection (SI) approach using extraction chromatography (two TEVA columns) was established for separation of technetium from interference. The automated separation setup consists of a FIALab-3500B SI system (FIALab Instruments, Bellevue, WA) furnished with a syringe pump (SP), a holding coil (HC), an internal 6-port multiposition selection valve (SV-1), four external 10-port multiposition selection valves (SV-2, SV-3, SV-4, and SV-5), and two separation columns (SC-1 and SC-2). A schematic illustration of the SI system is shown in Figure 2.

The separation procedure using two TEVA extraction chromatographic columns consists of the following steps: (i) rinsing the holding coil (HC) with 50 mL of deionized water and washing the sample inlet and outlet tubing with 0.1 mol/L HNO_3 at a flow rate of 5 mL/min; (ii) loading the sample solution (40–60 mL in 0.1 mol/L HNO_3 media) onto the first

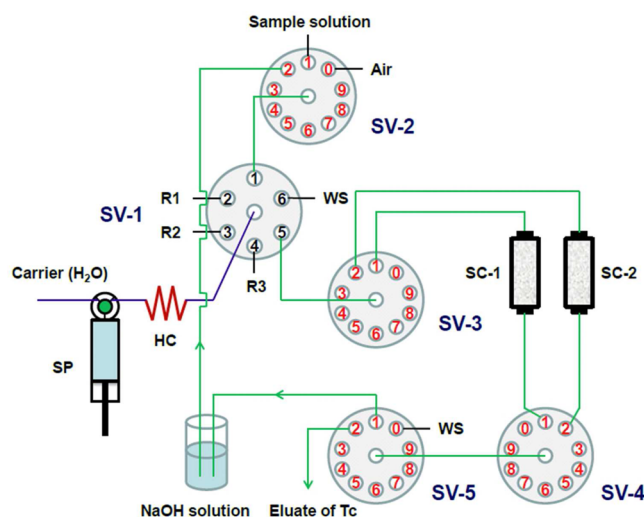


Figure 2. Schematic diagram of the sequential injection system for separation of ^{99}Tc from the sample matrix. R1: 0.1 mol/L HNO_3 ; R2: 1 mol/L HNO_3 ; R3: 8 mol/L HNO_3 ; WS: waste; SC: separation column (TEVA resin, 1.5 mL); air: port for air aspiration to isolate the carrier from the solution drawn into the holding coil; SP: syringe pump; SV: selection valve; HC: holding coil.

TEVA column at 1.0 mL/min; (iii) washing the column with 40 mL of 1 mol/L HNO_3 at 1.0 mL/min; (iv) eluting technetium from the column with 10 mL of 8 mol/L HNO_3 at 1.0 mL/min, the eluate is directly collected into a vial in which NaOH solution was pre-filled to obtain a final solution in 0.1 mol/L HNO_3 , and this solution was mixed through aspiration and injection of the solution using the syringe pump; (v) loading the obtained solution onto the second TEVA column at 1.0 mL/min; (vi) washing the column with 40 mL of 1 mol/L HNO_3 at 1.0 mL/min; (vii) eluting technetium from the column with 10 mL of 8 mol/L HNO_3 at 1.0 mL/min.

The eluate obtained from the second TEVA column was evaporated to dryness at 70–90 $^{\circ}\text{C}$ on a hot plate. The residue was dissolved in 0.5 mol/L HNO_3 and transferred to a 10 mL plastic tube (containing $^{115}\text{In}(\text{III})$ in an amount to make a final concentration of 1.0 $\mu\text{g/L}$, as an internal standard for the ICP-MS measurement of ^{99}Tc) and $^{99\text{m}}\text{Tc}$ in the solution was measured by NaI γ detector to monitor the chemical yield.

Measurement of ^{99}Tc by ICP-MS. The concentration of ^{99}Tc was measured by an ICP-MS system (X Series II, Thermo Fisher Scientific, Waltham, MA) equipped with an Xs-skimmer cone and standard concentric nebulizer. Prior to sample measurement, the ICP-MS instrument was tuned to optimize the ^{99}Tc signal using a ^{99}Tc standard solution (0.1 $\mu\text{g/L}$). A typical response for ^{99}Tc ranges from 1×10^5 to 3×10^5 cps per $\mu\text{g/L}$.

RESULTS AND DISCUSSION

Preconcentration of Technetium Using Coprecipitation. Coprecipitation using ferrous hydroxide is an effective and easy operation method to preconcentrate technetium in environmental water samples.^{5,26} In this method, the amount of iron added as carrier is critical to the yield of technetium and its chromatographic separation in the following steps. The results (Figure 3) show that chemical yields of technetium in the coprecipitation step increase from 5% to 85% with an increase in the amount of iron from 0.01 to 0.8 g, and a constant yield is observed for more than 0.8 g iron when processing a 50 L

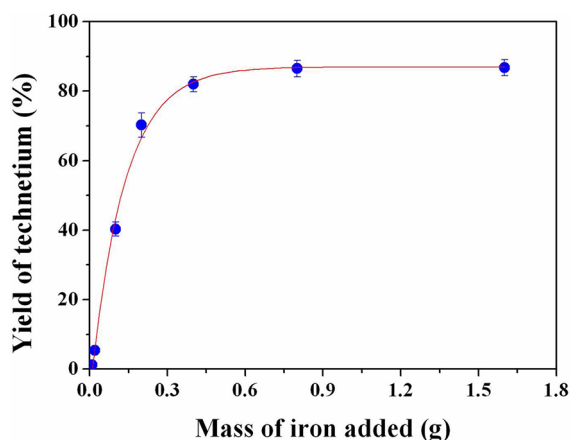


Figure 3. Effect of iron amounts on the coprecipitation separation of technetium from seawater samples, obtained using 50 L seawater samples following a reduction time of 30 min. The results are presented as the average \pm 2 SD of three replicates.

seawater sample and using $\text{NH}_3 \cdot \text{H}_2\text{O}$ to adjust the pH to 8–9. These results indicate that most of technetium (>85%) can be coprecipitated by $\text{Fe}(\text{OH})_2$ with an iron amount of 0.8 g for 50 L seawater samples (16 mg/L).

For such a large sample as 200 L of seawater, according to the study above, 3.2 g of iron should be added. Because the increase in the amount of iron will cause difficulty in following chromatographic separation of technetium, 0.8 g of Fe^{3+} was used for 200 L seawater samples in the present work. However, it was observed that only about 70% of technetium can be coprecipitated with $\text{Fe}(\text{OH})_2$, which indicates that the amount of the formed $\text{Fe}(\text{OH})_2$ is not enough to “carry” all technetium in such a large volume of seawater. The concentrations of alkaline earth elements are high in seawater (e.g., 1.3 g/L magnesium), and some of them can form precipitates at higher pH (e.g., $\text{Mg}(\text{OH})_2$). It was observed that when a high concentration of NaOH (e.g., 6 mol/L) was added to seawater to adjust the pH to 9–10, some white precipitates formed but not in the case when using $\text{NH}_3 \cdot \text{H}_2\text{O}$ to adjust the pH. This is mainly because of the much higher concentration of OH^- in 6 mol/L NaOH compared with concentrated $\text{NH}_3 \cdot \text{H}_2\text{O}$ which is a weak base with a pH around 13. The high concentration of OH^- results in the formation of $\text{Mg}(\text{OH})_2$, which is not easily dissolved in neutral and alkaline solution.²⁷ Although $\text{Mg}(\text{OH})_2$ shows a weak coprecipitation ability for technetium, some technetium can still be carried by $\text{Mg}(\text{OH})_2$ from the sample solutions (about 35% for 200 L of seawater; data are not shown) because of the large amount of Mg^{2+} present in seawater, resulting in a notable amount of $\text{Mg}(\text{OH})_2$ precipitate in the sample solution. Our results indicate that the chemical yield of technetium can be improved when both $\text{Fe}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ were precipitated by adding NaOH solution to a pH of 9–10 (>85% for 200 L seawater sample). Following this procedure, the volume of seawater sample can be reduced to less than 50 L with a high chemical yield (>85%). On the basis of this finding, it is recommended that for large volume seawater samples (e.g., 200 L), after Fe^{3+} and reductant are added, the pH of the sample solution should be first adjusted using NaOH solution to 9–10 to form $\text{Fe}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ precipitates in which technetium is coprecipitated. Then the precipitate is dissolved again, and $\text{NH}_3 \cdot \text{H}_2\text{O}$ is added to the

solution to form only $\text{Fe}(\text{OH})_2$ precipitate for further preconcentration of technetium.

$\text{K}_2\text{S}_2\text{O}_5$ was used to reduce technetium to Tc^{4+} in the present work. Effect of reduction time on the chemical yield of technetium was investigated (Figure 4). The results show that

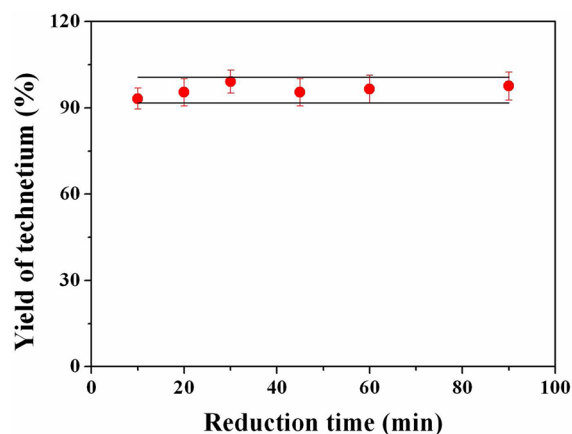


Figure 4. The chemical yield of technetium in a coprecipitate with ferrous hydroxide from seawater samples as a function of reduction time after the addition of $\text{K}_2\text{S}_2\text{O}_5$ (1.0 g/L). The results are presented as the average \pm 2 SD of three replicates, and the lines show the upper and lower values of 2 SD of mean value for all measured data.

the reduction of technetium and iron is quite rapid, and the reaction can be completed within 10 min, reflected by a constant chemical yield of technetium with the increase in reaction time from 10 to 90 min (Figure 4). The change in the solution color from brown to almost colorless suggests that Fe^{3+} was reduced to Fe^{2+} completely which in turn indicates that TcO_4^- is also reduced to Tc^{4+} because of the slightly higher redox potential of $\text{TcO}_4^-/\text{Tc}^{4+}$ (0.782 V) compared with $\text{Fe}^{3+}/\text{Fe}^{2+}$ (0.771 V). For large volume water samples, a 30 min reduction time was employed in our procedure for facilitating the operation and ensuring sufficient reduction of technetium.

Effect of $[\text{H}^+]$ and $[\text{NO}_3^-]$ on the Sorption of TcO_4^- onto TEVA Resin. Extraction chromatography using TEVA resin for the separation of technetium from the sample matrix and interference is based on a high affinity of TcO_4^- to TEVA resin.^{28,29} The distribution coefficient (K_d) of TcO_4^- onto TEVA resin decreases with increasing HNO_3 concentration; this is explained by ion exchange reaction,³⁰ that is, the elution of TcO_4^- from the TEVA column using a high concentration of HNO_3 is implemented through competition of NO_3^- with TcO_4^- on the functional groups of the resin's exchangeable sites. On the basis of this assumption, the concentration of NO_3^- in the loading solution will be the key factor affecting the sorption of TcO_4^- onto TEVA resin, consequently affecting the chemical yield of technetium in extraction chromatographic separation using the TEVA column. In previously reported methods, the sample solution loaded onto the TEVA column was often in a low concentration of HNO_3 media (less than 0.1 mol/L),^{19,31} while our preliminary experiment shows that TcO_4^- can be still adsorbed on the TEVA column even in 6 mol/L NaNO_3 without significant loss of TcO_4^- .

By investigating the influence of both $[\text{H}^+]$ and $[\text{NO}_3^-]$ on the sorption of TcO_4^- onto TEVA resin, it was observed that the K_d values of TcO_4^- decreases with increasing $[\text{HNO}_3]$ and $[\text{NaNO}_3]$ from 0.5 mol/L to 6 mol/L (Figure 5). A

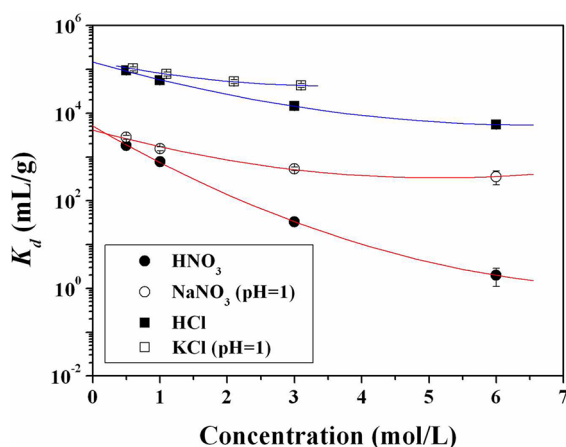


Figure 5. Effects of concentrations of $[\text{HNO}_3]$, $[\text{NaNO}_3]$, $[\text{HCl}]$, and $[\text{NaCl}]$ on the sorption of TcO_4^- onto TEVA resin, obtained at room temperature, an equilibrium time of 3 h, and a solid-to-liquid ratio of 20 g/L. The results are presented as the average ± 2 SD of three replicates.

significantly higher K_d value (about 500) is obtained for the NaNO_3 solution compared with HNO_3 media (about 2) with the same NO_3^- concentration of 6 mol/L (Figure 5), and the sorption of TcO_4^- is remarkably reduced when enhancing the concentration of HNO_3 from 0.5 mol/L to 6 mol/L, causing a tremendous decrease of K_d of TcO_4^- on TEVA resin from 2000 to 2. This observation indicates that $[\text{NO}_3^-]$ is not the only factor controlling the sorption of TcO_4^- onto TEVA resin, $[\text{H}^+]$ is another key parameter, probably the dominant factor for desorption of TcO_4^- from the TEVA column in the eluting process using a high concentration of HNO_3 . In addition, 5 times lower K_d of TcO_4^- in HCl media (about 1×10^4) is observed compared with that in KCl media (about 5×10^4) in the same concentration of Cl^- (3 mol/L), while a slightly decreased K_d from 1×10^5 to 5×10^4 is obtained when increasing the KCl concentration from 0.6 mol/L to 3.1 mol/L (Figure 5). This experiment confirms that $[\text{H}^+]$ is the main factor affecting the sorption of TcO_4^- onto TEVA resin. Compared with HNO_3 media, the K_d values of TcO_4^- in HCl media are much higher, which is mainly due to the different affinities of NO_3^- and Cl^- to TEVA resin. A higher relative affinity of NO_3^- (65) to strong base anion exchange resins compared with that of Cl^- (22) has been reported.³² TEVA has functional groups similar to that of strong base anion exchange resin; therefore a higher affinity of NO_3^- and a stronger competition with TcO_4^- on the TEVA resin is expected compared with that of Cl^- under the same conditions.

On the basis of these findings, the possible mechanism controlling TcO_4^- sorption onto TEVA resin at different concentrations of H^+ can be deduced. At low $[\text{H}^+]$, technetium mainly exists in the form of TcO_4^- , which shows a high

sorption to TEVA resin, indicated by a high K_d value for technetium. With increasing $[\text{H}^+]$, the formation of the neutral molecule HTcO_4 becomes dominant, which leads to a decreased concentration of TcO_4^- anion in solution, causing a low K_d value for technetium. Although the sorption of TcO_4^- onto TEVA is stronger compared with NO_3^- , the replacement of TcO_4^- from the resin by NO_3^- can occur when NO_3^- concentration is increased. In conclusion, elution of TcO_4^- from the TEVA column with a high concentration of HNO_3 is based on two factors, formation of HTcO_4 and replacement of TcO_4^- by NO_3^- , the former being dominant.

Online Separation of Technetium Using a Sequential Injection Extraction Chromatographic System. Because the concentrations of ruthenium (about 1 ng/L) and molybdenum (about 10 000 ng/L) in seawater are higher by about 10^3 folds for ruthenium and 10^7 fold for molybdenum compared with that of ^{99}Tc , the interference from the isobaric ^{99}Ru and molecular ion $^{98}\text{Mo}^1\text{H}$ is very serious for ^{99}Tc measurement using ICP-MS if ruthenium and molybdenum are not sufficiently removed. In this work, two TEVA columns were employed to separate and purify technetium from the interference in large volume seawater (e.g., 200 L), implemented through a sequential injection system. It is observed that chemical yields of technetium decreased with a decreasing amount of TEVA resin (ranged from 1.5 to 0.3 mL), and only 20% of technetium was recovered after column separation when using a 0.3 mL TEVA column (Table 1). This is attributed to a reduced sorption capacity of TEVA resin for TcO_4^- in a solution containing other competitive ions, especially when dealing with large sized environmental samples (e.g., 50–200 L of seawater). Although the majority of matrix elements have been removed during preconcentration of technetium from a large volume of seawater, the concentration of the remaining ions is still high to saturate the exchangeable sites on the small amount of resin and consequently reduces the sorption ability of the sorbent for TcO_4^- . In addition, 40 mL of 1 mol/L HNO_3 was used to wash the column; this might desorb some technetium from the TEVA resin thus causing a low chemical yield of technetium. Compared with environmental seawater samples, the chemical yields of technetium are much higher (above 80%) even for a small size of column (0.3 mL TEVA resin) if a 0.1 mol/L HNO_3 solution with spiked $^{99\text{m}}\text{TcO}_4^-$ was analyzed. These results indicate that desorption of technetium is not significant during the washing stage, while the matrix elements are the main factor reducing chemical yields of technetium during chromatographic separation.

Because of similar chemical properties, most of the molybdenum and ruthenium follow technetium during the preconcentration and are enriched together with technetium in the loading solution. For large volume seawater samples (e.g., 200 L), the results (Figure 6) show that one small TEVA column (1.5 mL resin) is not enough to quantitatively remove molybdenum and ruthenium, reflected by a relatively high

Table 1. Effect of Size of the TEVA Column on the Separation of Technetium (flow rate: 1 mL/min)^a

loading solution	chemical yield (%) of technetium on extraction chromatographic separation using different sizes of TEVA resin				
	0.3 mL	0.5 mL	0.7 mL	1.0 mL	1.5 mL
seawater sample (pH \approx 1)	20.1 \pm 1.5	46.3 \pm 1.9	70.5 \pm 2.1	88.3 \pm 2.5	96.4 \pm 2.7
0.1 mol/L HNO_3 solution	81.6 \pm 2.0	82.4 \pm 2.8	89.3 \pm 2.4	95.7 \pm 2.2	98.2 \pm 1.9

^aThe seawater sample (50 L) was treated for preconcentration of technetium by coprecipitation using iron hydroxide before column separation; results are given as the average ± 2 SD of the three replicates.

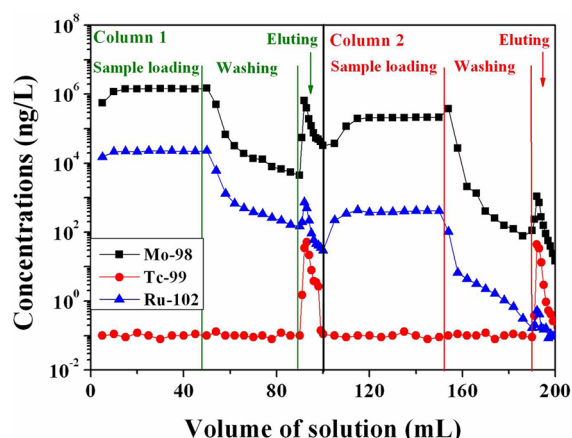


Figure 6. Sorption and elution behaviors of technetium, ruthenium, and molybdenum in extraction chromatographic separation using two small TEVA columns (1.5 mL for each). The sample solutions (50 mL) were adjusted to pH 1 with 8 mol/L HNO_3 before loading; the column was washed with 40 mL of 1 mol/L HNO_3 , and the analytes were eluted with 10 mL of 8 mol/L HNO_3 .

concentration of these two elements in the eluate from the first column. The decontamination factors for molybdenum and ruthenium are less than 10^3 and the signal of technetium at mass 99 receives serious interference from ^{99}Ru and $^{98}\text{Mo}^1\text{H}$. With two TEVA columns, almost all the ruthenium and most of the molybdenum can be removed while technetium is still retrieved in a high chemical yield (Figure 6). The obtained overall decontamination factors of ruthenium and molybdenum are better than 1×10^6 and 5×10^5 , respectively, for large volume seawater samples (>50 L) with chemical yields of technetium ranging from 60% to 75% (Table 2).

It should be noted that there is still considerable amounts of molybdenum (about 10 times higher than technetium by mass) present in the final eluate, which is measurable by ICP-MS (Figure 6). However, the interference from $^{98}\text{Mo}^1\text{H}$ at this level with ^{99}Tc is negligible because the measured $^{98}\text{Mo}^1\text{H}/^{98}\text{Mo}$ ratio ($\approx 10^{-4}$) under the measurement conditions is very low, and $^{99}\text{Tc}/^{98}\text{Mo}^1\text{H} > 10^3$ was measured in this work. The concentration of ruthenium is relatively low in the final eluate (Figure 6), and the $^{99}\text{Ru}/^{99}\text{Tc}$ ratio is less than 0.01. Consequently, interference from $^{98}\text{Mo}^1\text{H}$ and ^{99}Ru is eliminated using the present procedure.

Detection Limit and Duration of the Established Method. Because of the sufficient removal of molybdenum and ruthenium by the present procedure, a detection limit (based on 3 times the standard deviation of signal of the procedure blank) of 7.5 mBq/m^3 (or 11.5 pg/m^3) for 200 L of seawater has been obtained in this work, which is much lower than the values reported in the literature using ICP-MS (250 mBq/m^3 for 5–30 L of water)³³ and the radiometric method

using LSC (600 mBq/m^3 for 200 L of water)³⁴ and at the same level as the reported values obtained by β -counting using a low level gas flow GM counter (3 mBq/m^3 for 500 L of water).¹³

The analytical time is remarkably reduced when the automated system using the sequential injection approach and the optimized preconcentration procedure are applied. A batch of seawater samples ($n > 4$) can be analyzed within 24 h, which is much shorter than that reported previously for the conventional method (usually 2–3 days).¹³ Consequently, the problem caused by the short half-life of $^{99\text{m}}\text{Tc}$ ($T_{1/2} = 6.06 \text{ h}$) tracer during the analytical process can be solved. Therefore, rapid determination of low level ^{99}Tc in seawater samples can be achieved.

Analysis of Seawater Samples Collected from Danish Waters. Standard reference material used to verify the reliability of new analytical methods for ^{99}Tc in large volume seawater samples is not available. To assess the accuracy and applicability of the developed method, seawater samples collected at Klint, Denmark, were analyzed using the developed method, and the results were compared with the ones obtained by the conventional method using anion exchange chromatographic preconcentration, solvent extraction, and precipitation separation followed by low level gas flow GM counter measurement.³⁵ The analytical results (Table 2) show that the measured ^{99}Tc concentrations in seawater samples by the present method agree well with the values determined by the conventional method;³⁵ meanwhile, good chemical yields of technetium in the overall procedure ($>60\%$) and sufficiently high decontamination factors for Ru and Mo ($>5 \times 10^5$) were obtained. This indicates that the present analytical method is reliable and accurate for the determination of ^{99}Tc in large volume seawater samples.

CONCLUSIONS

ICP-MS coupled with an online chromatographic separation using a sequential injection approach was applied successfully to determine ^{99}Tc in large volume seawater samples. On the basis of the work presented above, the following conclusions can be drawn: (i) Technetium can be concentrated effectively by an optimized procedure based on coprecipitation using ferrous hydroxide from large volume seawater samples. (ii) Matrix elements of the sample affect the sorption of TcO_4^- to TEVA resin. With the application of two small TEVA columns (1.5 mL for each), decontamination factors of $>10^6$ for ruthenium and $>10^5$ for molybdenum and recovery of $>60\%$ for technetium were achieved for up to 200 L seawater samples, reaching a detection limit of 7.5 mBq/m^3 (or 11.5 pg/m^3). (iii) The concentration of H^+ is the main factor affecting the sorption of TcO_4^- onto TEVA resin. The elution of TcO_4^- from the TEVA column with a high concentration of HNO_3 might be attributed to the formation of HTcO_4 at high $[\text{H}^+]$ and the replacement of TcO_4^- by NO_3^- , in which the

Table 2. Analytical Results of ^{99}Tc in a Seawater Sample Using the Developed Method and Conventional Method^a

seawater sample (L)	chemical yield (%)	^{99}Tc measured (mBq/L)	decontamination factors		^{99}Tc measured by conventional method ^b (mBq/L)
			Mo	Ru	
50	68–75	0.270 ± 0.018	$(5.6 \pm 0.8) \times 10^5$	$(1.4 \pm 0.6) \times 10^6$	—
200	60–70	0.265 ± 0.021	$(7.0 \pm 1.2) \times 10^5$	$(7.7 \pm 1.5) \times 10^6$	0.267 ± 0.016

^aResults are given as the average ± 2 SD of three replicates. ^bValues were obtained using the method reported by Chen et al.³⁵ The chemical yield of technetium in this method was 70–80%.

formation of HTcO_4 is dominant factor. (iv) With the sequential injection approach employing two small TEVA columns (1.5 mL for each) and ICP-MS measurement, the developed method remarkably reduced the analytical time, and a batch of samples ($n > 4$) can be analyzed within 24 h. (v) The analytical procedure is validated by analysis of the same seawater samples using a conventional method and can be used for the determination of low level ^{99}Tc in environmental aqueous samples.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

K. Shi appreciates the staff in the Radioecology and Tracers Programme (headed by Sven P. Nielsen), DTU Nutech, for their help during the experiment, as well as China Scholarship Council for the partial financial support to his Ph.D. project.

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Paper IV

Shi, K.L.; Hou, X.L.; Roos, P.; Wu, W.S.; Nielsen S.P.

Seasonal variation of technetium-99 using *Fucus vesiculosus* as its application as oceanographic tracer

(Submitted to Estuarine, Coastal and Shelf Science)

Seasonal variation of technetium-99 using *Fucus vesiculosus* as its application as oceanographic tracer

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ABSTRACT

The concentration of ⁹⁹Tc was determined in archived time series seaweed samples collected at Klint (Denmark). The results demonstrate a significantly seasonal variation of ⁹⁹Tc concentrations in *Fucus vesiculosus* with maximum values in winter and minimum values in summer. The mechanism driving this seasonal cycle was explored. With the measured ⁹⁹Tc concentration in seawater collected in the same location and date as for seaweed, the concentration factor of *Fucus vesiculosus* to ⁹⁹Tc was investigated. Quite constant value of concentration factors of ⁹⁹Tc independence of sampling date, with an average value of $(1.9 \pm 0.5) \times 10^5$ L/kg, were obtained. This indicates that *Fucus vesiculosus* can be used as a reliable bio-indicator to monitor ⁹⁹Tc concentration in seawater.

Keywords: Technetium-99, seaweed, seawater, seasonal variation, concentration factor

1. Introduction

The presence of technetium-99 (⁹⁹Tc) in the marine environment is principally due to the discharges of radioactive effluents from reprocessing plants, mainly from two European reprocessing plants at Sellafield (UK) and La Hague (France), as a result of the chemical processing of spent nuclear fuel (Calmet et al., 1987). Because of the long half-life ($T_{1/2} = 2.13 \times 10^5$ y) as well as long residence time (technetium is assumed to occur in open seawater in the form of TcO_4^-), ⁹⁹Tc has been used as an oceanographic tracer to track seawater movement and coastal pollution (Aarkrog et al., 1988). The transport of ⁹⁹Tc from western European reprocessing plants to distant sea areas, especially to Nordic seas has been a topic of extensive research in the last few decades (Aarkrog et al., 1988; Masson et al., 1995; Dahlggaard et al., 1995; Brown et al., 2002).

For this purpose, temporal and spatial variations of ⁹⁹Tc in seawater have to be investigated, which requires accurate determination of ⁹⁹Tc in seawater samples. Due to the very low concentration of ⁹⁹Tc in seawater which is not directly exposed to nuclear discharges/contamination (< 5 mBq/L), a large volume seawater sample (e.g., 50-200 L) is usually needed to obtain an accurate concentration of ⁹⁹Tc. Considering collection and transport of large volume seawater samples, the analysis of ⁹⁹Tc in seawater is very expensive and laborious. As commonly brown seaweeds in European coast, *Fucus* genus especially *Fucus vesiculosus* and *Fucus serratus* show very high capacities to accumulate ⁹⁹Tc from seawater, and thus have been considered to be ideal bio-indicators of radioactive contamination in coastal regions, especially for investigation of temporal variation and spatial distribution of ⁹⁹Tc in seawater, because of easy sample collection, transport and especially long-term storage (Aarkrog et al., 1987; Keogh et al., 2007; Nawakowski et al., 2004).

The accumulation capacity of a species of seaweed to ⁹⁹Tc in marine environment can be characterized by its

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concentration factor (CF), which is defined as ^{99}Tc concentration in seaweed (Bq/kg dry weight) divided by ^{99}Tc concentration in seawater (Bq/L). With a known value of the concentration factor, the concentration of ^{99}Tc in seawater can be calculated if the concentration of ^{99}Tc in seaweed (collected at the same location as the seawater) is determined. This is an effective way to evaluate ^{99}Tc concentrations in seawater without analyzing large volume seawater samples.

By analysis of time series of seaweed samples, researchers have successfully evaluated early discharges of radionuclides from reprocessing facilities, which in turn indicates the general circulation of the ocean currents (Dahlgaard et al., 1997; Hou et al., 2000). However, the application of seaweed as a bio-indicator to estimate the concentration of ^{99}Tc in seawater is based on an assumption that the concentration factor of ^{99}Tc in specific species of seaweed is a constant value and does not vary with sampling date. According to the studies by Calmet et al. (1987) and Patti et al. (1990), the concentrations of ^{99}Tc in *Fucus serratus* show a significantly seasonal variation with higher concentrations in winter and lower concentrations in summer. To this point, if the seasonal variation of ^{99}Tc in seaweed is a common phenomenon, and is controlled by biological metabolism of the seaweed, a correction for seasonal variation of concentration factor should be carried out while investigation on the time series of ^{99}Tc in seawater, otherwise unreliable conclusions and mis-explanations might be given. Therefore an investigation on the seasonal variation of ^{99}Tc in seaweed and its mechanism is important for the application of ^{99}Tc as an oceanographic tracer. To our best knowledge, studies on this topic, especially on the mechanism of seasonal variation of ^{99}Tc in seaweed are still very rare. In addition, although similar concentration factors of ^{99}Tc in brown seaweed *Fucus vesiculosus* have been reported (Smith et al., 2001; Aarkrog et al., 1987), the values are still not representative because they are usually obtained using limited numbers of data on concentration of ^{99}Tc in seaweed and seawater. Accordingly, a comprehensive investigation on the concentration factor of ^{99}Tc in seaweed for exploring its temporal variation is needed.

This work aims to investigate the seasonal variation of ^{99}Tc concentration in time series of seaweed and seawater to determine the concentration factor of ^{99}Tc in *Fucus vesiculosus*, as well as to explore the mechanism driving the seasonal variation of ^{99}Tc concentration in seaweed.

2. Materials and methods

2.1. Materials

A ^{99}Tc standard solution (in NH_4TcO_4 form, 4.17 Bq/g) was supplied by Risø National Laboratory, Technical University of Denmark. $^{99\text{m}}\text{Tc}$ tracer was obtained from 2-4 GBq commercial ^{99}Mo - $^{99\text{m}}\text{Tc}$ generators (Amersham, UK) and purified using alumina cartridges according to the method reported by Hou et al. (Hou et al., 2007). All other reagents used in the experiment were of analytical grade and prepared using deionized water (18.2 MΩ·cm). Anion exchange chromatography (AG1- \times 4 resin, 100-150 μm particle size, Bio-Rad Laboratory, USA) was used to concentrate technetium from large volume seawater samples.

Time series of seaweed (*Fucus vesiculosus*) and seawater samples were collected at Klint (55°58' N, 11°34' E, Kattegat, Denmark) in the years of 1991-2008 (except 1993-2000 for seawater samples). The sampling location (Klint) is shown in Fig. 1. The seaweed samples were dried at 80-100°C and archived until analysis. Seawater samples were filtered through a 0.45 μm membrane filter and analyzed within 6 months.

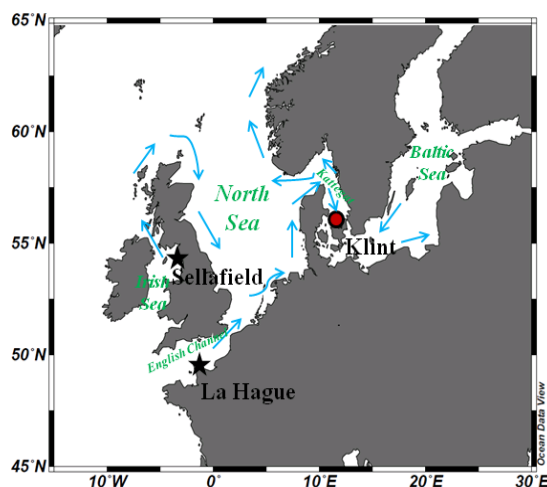


Fig. 1. Sampling location of seaweed and seawater at Klint, and the main water currents in the North Sea leading activity from Sellafield and La Hague to Kattegat (Denmark).

2.2. Analytical methods

Seawater and seaweed samples collected at Klint, Denmark were analyzed using the procedures reported by Chen et al. (2001), which is briefly described below.

Seawater analysis

The filtered seawater was spiked with ^{99m}Tc as a yield monitor, pre-concentrated using anion exchange chromatography (AG1- \times 4 resin), and further purified using solvent extraction (5% tri-isooctylamine (TIOA)-xylene). After the source preparation using electrodeposition, the activity of ^{99}Tc was measured using an anti-coincidence gas flow Geiger-Muller (GM) counter (Risø, Denmark). The chemical yields of technetium in whole procedure were measured by counting ^{99m}Tc tracer using a NaI γ -ray detector.

Seaweed analysis

For seaweed samples, after spiking with ^{99m}Tc as a yield monitor, a wet ashing method using concentrated H_2SO_4 carbonation and acid digestion was applied to decompose seaweed, and then followed the same procedure as for seawater for ^{99}Tc determination.

3. Results and discussion

3.1. Transit time

The transit time is defined as the interval between a specific discharge event and the occurrence of the signal of this event at the sampling points (Dahlggaard et al., 1995). It can be estimated by correlation analysis of discharge history of a radionuclide with the measured concentration of this nuclide in time series of samples collected at the investigated location. In this work, ^{99}Tc concentrations in time series brown seaweed (*Fucus vesiculosus*) sampled at Klint (Denmark) during 1993-2008 have been determined. The results (Fig. 2) show that the ^{99}Tc concentration increased steadily from 1997, and reached a maximum value around the years of 1999-2000. Compared with the discharges of ^{99}Tc from Sellafield reprocessing plant (Fig. 2(A)), the signal “peak” of ^{99}Tc in *Fucus vesiculosus* was delayed about 3.5-4.5 years relative to the discharge signal (Fig. 2(B)),

indicating the transit time of seawater from the Irish Sea (Sellafield discharge point) to Klint is approximately 3.5-4.5 years. This is in good agreement with earlier estimation by Hou et al. (2000), in which a transit time of 3.8 years from Sellafield to Klint was estimated using ^{129}I as an oceanographic tracer.

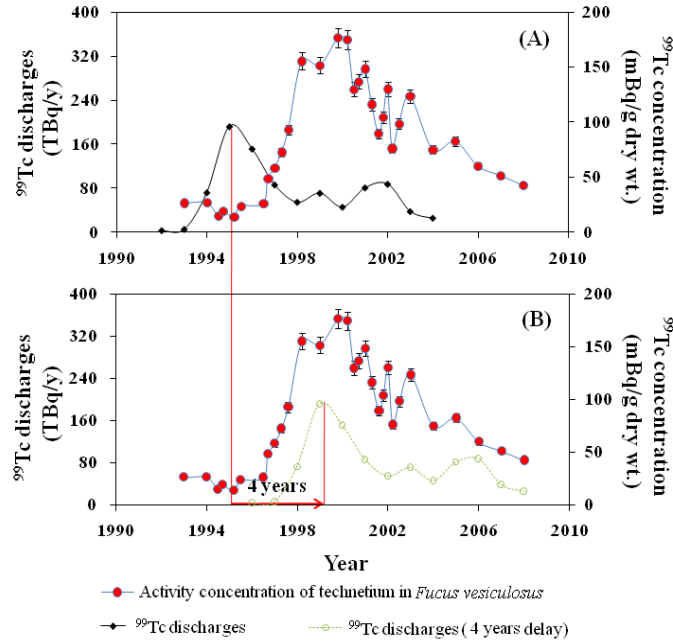


Fig. 2. A comparison of “smoothed” ^{99}Tc discharges from Sellafield with ^{99}Tc concentration in time series of *Fucus vesiculosus* collected at Klint: (A) ^{99}Tc discharges data from Sellafield reprocessing plant; (B) shifted ^{99}Tc discharge data with 4 years delay. The experimental results are presented as the average value \pm 2SD of the three replicates.

3.2. Seasonal variation of ^{99}Tc in seaweed

A seasonal cycle of ^{99}Tc concentration in *Fucus vesiculosus* collected monthly at Klint (Denmark) was observed. The variation trend of ^{99}Tc concentrations is similar as the reported variation of the concentrations of iodine-127 (^{127}I) and potassium-40 (^{40}K) in *Fucus serratus* (Patti et al., 1990), i.e. maximum value in winter and minimum value in summer (Fig. 3), although the extent of variation of ^{99}Tc concentrations is smaller than that of ^{127}I and ^{40}K . Several factors including the variation of the temporal discharges of ^{99}Tc from reprocessing plants, biological processes (cycle) in seaweed, and environmental processes such as dilution of ^{99}Tc in contaminated seawater by uncontaminated water, might affect ^{99}Tc concentration in seaweed and result in seasonal fluctuation of ^{99}Tc concentration.

Concentrations of elements in plants are usually related with biological processes such as plant growth (Patt et al., 1990). Accordingly, the concentration of ^{99}Tc might decrease during fast growth of seaweed in warm conditions, causing a lower concentration of ^{99}Tc in summer. Correspondingly, relatively high concentrations of ^{99}Tc might be observed in winter due to the slow growth of seaweed. However, according to the report by Hattink et al. (2000), the uptake of technetium in seaweed is relatively fast, and equilibrium of technetium between seawater and seaweed can be quickly reached. To this point, the effect of rapid growth of seaweed on the seasonal variation of technetium

concentration might be limited. The concentrations of ^{99}Tc in old and fresh parts of the seaweed should be similar after a suitable uptake period if other conditions such as the concentration of ^{99}Tc in seawater are the same. Of course, the distribution of technetium in seaweed is usually inhomogenous, higher level of ^{99}Tc in leaves and stems, and lower concentration in boluses have been observed (Table 1). This is mainly attributed to the different composition in different parts of seaweed. For example, higher water as well as salt content in bolus parts compared with the stem and leaf parts. If the seaweed sample contains more boluses, the concentration of ^{99}Tc will be lower compared with the same seaweed sample but with less boluses.

Table 1. Distribution of ^{99}Tc in different parts of seaweed (samples were collected at Hvide Sande, west coast of Denmark in 2012 and analyzed by our previously reported method (Shi et al., 2012a))

Different parts of seaweed	Concentration of ^{99}Tc (mBq/g dry wt.) *
Stems	30.2 ± 2.1
Leaves	24.7 ± 1.8
Boluses	18.7 ± 1.5

* The results are presented as the average \pm 2SD of the three replicates.

During the years of 1982-1991, most of ^{99}Tc in the European water originates from the La Hague reprocessing plant, while before and after these periods the discharges of ^{99}Tc from Sellafield reprocessing plant dominates (Shi et al., 2012b). For the monthly seaweed samples collected at Klint, Denmark in 1991-1992, the dominating source of ^{99}Tc is from La Hague reprocessing plant (Shi et al., 2012b). Although the monthly discharge of ^{99}Tc in the years of 1989-1990 is not available (the transit time is about 2 years from La Hague to Klint (Masson et al., 1995)), according to the report by Patti et al. (1990), there is no obvious seasonal cycle of ^{99}Tc discharges during the period of 1985-1988 in La Hague reprocessing plant, indicating that the discharges of ^{99}Tc from reprocessing plant do not significantly contribute to the seasonal variation of ^{99}Tc concentration in the seaweed from Kint during 1991-1992. Of course, as mentioned above, the increased discharges of ^{99}Tc increases the concentration of ^{99}Tc in seawater and accordingly in seaweed. Relatively high levels of ^{99}Tc observed in seaweed from Klint in the beginning of 1991 (Fig. 3) and after 1996 (Fig. 2) are due to the high marine discharges of ^{99}Tc from the reprocessing plants at La Hague and Sellafield, respectively.

The sampling location at Klint is located in the Kattegat, where contaminated seawater with high salinity from the North Sea is mixed with the less contaminated Baltic Sea water (low salinity) (see Fig.1). Therefore, the concentration of ^{99}Tc in seawater in this area (e.g., Klint) is significantly influenced by the exchange of water between the North Sea and the Baltic Sea (Holm et al., 1986), and a very good correlation between salinity and ^{99}Tc concentration in seawater from the Kattegat was observed, i.e. the higher concentration of ^{99}Tc with the higher salinity in seawater (Lindahl et al. 2003). In addition, because the seaweed samples were collected in coastal areas, the runoff of fresh water from the land will dilute the concentration of ^{99}Tc in seawater and consequently reduce ^{99}Tc concentration in seaweed although this effect might be not significant. Salinity of surface water collected in Kattegat in different seasons of 1990-2010 shows a clear seasonal cycle with higher salinities in winter and lower ones in summer (data are not shown), which is similar to the variation of ^{99}Tc concentrations in seaweed (Fig.3). Lower concentrations of ^{99}Tc in seaweed collected from the Klint in summer compared with those in the winter time might be caused by the dilution of ^{99}Tc concentration in the seawater in summer due to higher outflow of low ^{99}Tc concentration water from the Baltic Sea to Kattegat as well as the

higher precipitation rate during the summer time. A similar seasonal variation of ^{99}Tc in seawater collected at Klint in 1991-1992 was also observed in this work, i.e. a higher ^{99}Tc concentration in winter and lower in summer (Fig. 4), which confirms the above assumption that the seasonal variation of ^{99}Tc in seaweed is attributed to the concentration of ^{99}Tc in the seawater from which ^{99}Tc was uptaked.

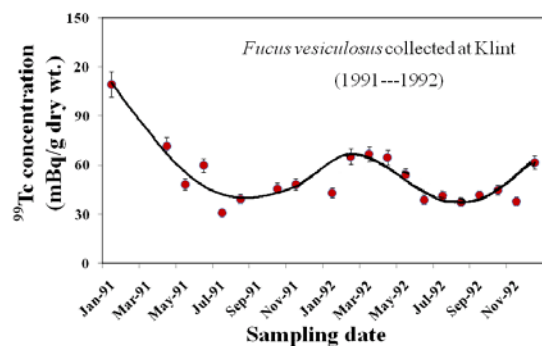


Fig. 3. Seasonal variation of ^{99}Tc concentrations in *Fucus vesiculosus* collected at Klint. The results are presented as the average value \pm 2SD of the three replicates.

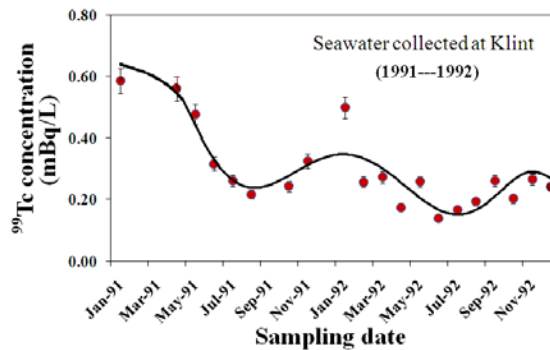


Fig. 4. Seasonal variation of ^{99}Tc concentrations in seawater collected at Klint. The results are presented as the average value \pm 2SD of the three replicates.

In summary, the seasonal variation of ^{99}Tc in seaweed can be caused by several factors including biological processes, discharges of ^{99}Tc in reprocessing plants, and environmental variation, among them, the environmental conditions such as seawater movement and water exchange might be dominant.

3.3. Concentration factors

According to Hou and Yan (1998), seaweed shows high accumulation capabilities to a wide variety of inorganic elements, especially trace elements. It is therefore often used as a bio-indicator to monitor the extent and rate of dispersion of contamination by measurement of some elements or artificial radionuclides such as ^{99}Tc . In particular, brown seaweeds such as *Fucus* genus (e.g., *Fucus vesiculosus*, *serratus* or *spiralis*) concentrate technetium from seawater with a high concentration factor in the order of 10^5 (Aarkrog et al., 1987; Nawakowski et al., 2004; IAEA, 2004). By measurement of ^{99}Tc concentrations in seawater and seaweed samples collected monthly in the same date during 1991-1992 at Klint, Denmark, concentration factors of ^{99}Tc in *Fucus vesiculosus* were calculated. The results (Fig. 5) show no significant variation of concentration factors of ^{99}Tc with sampling date, although significantly seasonal variations of ^{99}Tc concentration in seaweed and seawater were observed (Fig.5). Further investigation on concentration factors of ^{99}Tc in *Fucus vesiculosus* by analysis of time series of seawater and seaweed samples collected at Klint during 2000-2008 (Fig.6) indicates that the concentration factor of technetium is an intrinsic parameter for a specific seaweed and does not vary with sampling date. The measured concentration factor of ^{99}Tc ranges from 1.3×10^5 to 2.4×10^5 L/kg with a mean value and 2SD of $(1.9 \pm 0.5) \times 10^5$ L/kg. This value agrees with the previously reported values of $(1.75 \pm 0.21) \times 10^5$ L/kg (1SE of uncertainty) measured in *Fucus vesiculosus* collected from Klint (Denmark) (Masson et al., 1995), and $(1.32 \pm 0.46) \times 10^5$ L/kg (2SD of uncertainty) in *Fucus vesiculosus* collected in Irish coast in the Irish Sea (Smith et al. 2001). The relatively constant concentration factors of ^{99}Tc in *Fucus vesiculosus* measured in this work (Fig. 5 and Fig. 6) indicate the reliability to use *fucus vesiculosus* as a bio-indicator for estimation of ^{99}Tc concentration in seawater and further application of ^{99}Tc in seaweed for oceanographic tracer studies. Meanwhile, this also makes it simple to model the variation of ^{99}Tc concentration in seaweed based on the discharge data

of ^{99}Tc from reprocessing plants, and consequently its temporal variation and spatial distribution along the coastal area. The slightly high uncertainty for the reported concentration factors of ^{99}Tc is attributed to the relatively high analytical uncertainty of ^{99}Tc due to its very low concentration in seawater. This issue has to be considered when using the concentration factor to estimate ^{99}Tc concentration in seawater.

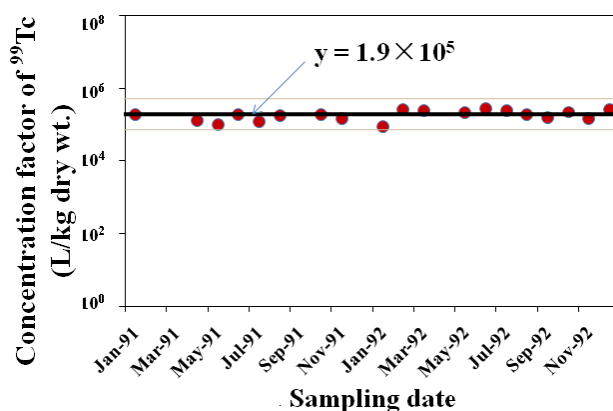


Fig. 5. Variation of concentration factors of ^{99}Tc in *Fucus vesiculosus* monthly collected in 1991-1992 at Klint, Denmark. The results are presented as the average value \pm 2SD, and the lines show the average and upper and lower values of 2SD of all experimental data.

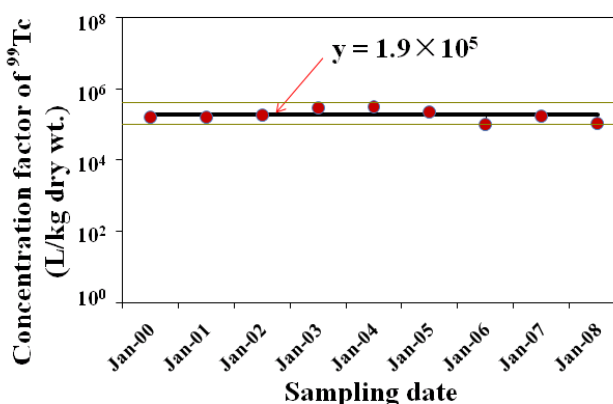


Fig. 6. Variation of concentration factors of ^{99}Tc in time series of *Fucus vesiculosus* collected in 2000-2008 at Klint, Denmark. The results are presented as the average value \pm 2SD, and the lines show the average and the upper and lower values of 2SD of all experimental data.

It should be mentioned that different species of seaweed show different concentration factors. Brown seaweeds, especially *Fucus* genus usually present relatively high accumulation abilities to radionuclides and thus have high concentration factors. For different *Fucus* species, an order of concentration factors of ^{99}Tc *Fucus vesiculosus* > *Fucus serratus* > *Fucus spiralis* has been reported (McCartney and Rajendran, 1997). The variation of concentration factors of ^{99}Tc with different species of seaweed might be attributed to their different biological function to uptake ^{99}Tc into the plant cells and the binding mode of technetium with the corresponding components. A further investigation on the uptake processes of ^{99}Tc by different types of seaweed, especially on the speciations of technetium in different seaweeds will be helpful to explain the mechanism controlling their accumulation to technetium.

4. Conclusions

Based on the analytical results and discussion above, it can be concluded that: (i) the concentrations of ^{99}Tc in *Fucus vesiculosus* collected at Klint (Denmark) have increased since 1997 following the increased discharges of ^{99}Tc from Sellafield reprocessing plant from 1994, a transit time of 3.5-4.5 years for the seawater from Sellafield to Klint is estimated based on the experimental data and the historic data of ^{99}Tc discharges from Sellafield reprocessing plant; (ii) the concentrations of ^{99}Tc in seaweed show a seasonal cycle with a higher concentration in winter and lower concentration in summer. Dilution of ^{99}Tc concentration in seawater by less contaminated water mass due to water exchange and movement as well as runoff of the fresh water from the land might be the main reason driving the seasonal variation of ^{99}Tc concentration in seaweed; (iii) concentration factors of ^{99}Tc in seaweed show a relatively constant value and are independent on sampling date. A mean concentration factor of $(1.9 \pm 0.5) \times 10^5$ L/kg dry weight for *Fucus vesiculosus* was obtained. This information is important for application of *Fucus vesiculosus* as a bio-indicator to monitor the pollution of seawater and estimate the temporal variation and dispersion of pollution in the marine system.

Acknowledgements

K. Shi appreciates the staff in the Radioecology and Tracers Programme (headed by Sven P. Nielsen), DTU Nutech, Technical University of Denmark for their help during the experiment, as well as China Scholarship Council for the partial financial support to his PhD. project.

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